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A New Correction in Viscometry by the Capillary-Tube Method

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The hydrostatic head correction as ordinarily made in viscosity measurements may be in error. This is made evident when one determines this correction at widely different pressures or with liquids of widely differing fluidities. It is concluded that this error is due to differences in the value of the coefficient m of the kinetic energy correction in different directions of flow. Such differences are due to departure of the capillary tube from a true cylinder which may have arisen in the manufacture of the capillary or of the viscometer. These differences in the value of m are so considerable that not only should the value of m for each viscometer be determined but a separate value should be determined for each direction of the flow through the capillary. Fortunately, this measurement is simple.

IN using the variable pressure viscometer[1] shown in Fig. 1, the corrected pressure p used in producing the flow is largely derived from external air-pressure admitted at will to either limb, but if the two bulbs, C and K in the figure, are not at the same level or differ in size or shape, there will be a hydrostatic head[2] correction h_1; and even if all of these conditions are met, there may be a so-called true average pressure correction[3] when the external pressure is not large in comparison with the height of the bulbs BD. The formula for calculating the viscosity η is generally accepted to be

$$\eta = \pi g p R^4 t/[8V(l+\lambda)] - m\rho V/[8\pi t(l+\lambda)] \quad (1)$$

where V is the volume flowing in t seconds through the capillary of length l and radius R. The second term of this equation is the kinetic energy correction containing the coefficient m which is sometimes incorrectly assumed to have a certain value, but which should be determined by direct measurement,[4] and ρ is the density of the fluid. Since the validity of the end correction λ is still a matter for debate,[5] it may be assumed

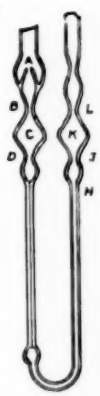

FIG. 1. Diagram of variable pressure viscometer.

[1] Bingham, Proc. A. S. T. M. **18**, Pt. II, 373 (1918); also U. S. Bur. of Standards, Bull. 298, **14** (1917).

[2] Hydrostatic head correction is calculated as follows: If h_1 is positive when the bulb K is higher than the bulb C, i.e., if $p_r > p_l$ and $t_r < t_l$, then $p_l = p - h_1\rho$ and $p_r = p + h_1\rho$. Hence from Eq. (2) with approximate values of C

$$C(p-h_1\rho)t_l - C'\rho/t_l = C(p+h_1\rho)t_r - C'\rho/t_r$$

and therefore

$$h_1 = [(t_l - t_r)(t_l + t_r)][p/\rho + C'/(Ct_l t_r)].$$

[3] Bingham, Schlesinger and Coleman, J. Am. Chem. Soc. **38**, 27 (1916).

[4] Bingham and Thompson, J. Rheology **1**, 418 (1930).

[5] Bingham, *Fluidity and Plasticity*, p. 21.

provisionally that λ is a constant for a given instrument, and therefore does not vary with the rate of flow nor with the direction of flow through the capillary. The above formula then reduces to the following form for the relative measurements now under discussion:

$$\eta = Cpt - mC'\rho/t, \qquad (2)$$

where C and C' are constants, and the latter is determined by direct measurement.

The work of Bingham and Thompson[4] showed that the value of m in these formulas is considerably affected by the shape of the entrance to the capillary. It was observed by Bingham and Arnold and no doubt by others that the rate of flow through a capillary is dependent upon the direction of flow, but no one seems to have pointed out the necessity which follows of making an additional correction in viscosity measurement.

TABLE I. *Values of C of viscometer 1−31 obtained by using low pressures with m = 1.12.*

Limb	p	t in seconds	C
L	50.12	1104.3	1.8187×10^{-7}
R	50.18	1103.8	1.8174
L	50.49	1096.7	1.8179
R	50.50	1096.2	1.8181
		Average C	1.8181×10^{-7}

The other corrections which have already been noted, particularly the hydrostatic head, make it more difficult to determine the m_l and m_r which are desired. The authors offer the following solution. With a viscometer with a long narrow capillary, the external pressure could be made large enough to keep the true average pressure correction inappreciable and still maintain so small a rate of flow that the kinetic energy correction could not be of influence even if the value of m departs widely from the customary 1.12. By assuming the viscosity of water to be 1.005 centipoises at 20°, the value of the hydrostatic head, $h_1 = 0.01$ cm, and the value of $C = 1.818 \times 10^{-7}$ were calculated from the data on flow obtained (Table I).

The external pressure was then increased and the measurements of the flow made in both directions; the values of m_l and m_r were calculated from the values of h_1 and C already known. The correctness of the method was made certain by calculating C (Table II) for experiments at higher pressures for each limb, cleaning out the instrument and refilling with water and with other liquids thus obtaining different experimental data. Table III shows that the coefficient for the left limb is invariably larger than that for the right limb, although there was no reason for the difference apparent to the eye.

TABLE II. *Comparison of values of C by using (A) $h_1 = +0.25$ cm and $m_l = m_r = 1.12$, and (B) corrected values $h_1 = +0.01$, $m_l = 1.46$ and $m_r = 0.74$.*

Sample*	Limb	Pressure	*A*	*B*
No. 2	L	197.65	1.8166×10^{-7}	1.8178×10^{-7}
	R	197.67	1.8192	1.8175
	L	197.66	1.8165	1.8177
	R	197.67	1.8185	1.8169
	R	102.53	1.8159	1.8181
	L	102.71	1.8198	1.8174
	R	102.83	1.8160	1.8182
	L	102.88	1.8199	1.8174
No. 3	L	202.09	1.8149	1.8162
	R	202.11	1.8210	1.8192
	L	202.09	1.8155	1.8169
	R	202.11	1.8210	1.8192
	L	102.81	1.8214	1.8190
	R	102.92	1.8157	1.8180
	L	102.94	1.8208	1.8184
	R	102.98	1.8164	1.8186
		Average	1.8182×10^{-7}	1.8179×10^{-7}

* The two samples used were pure, distilled, dust-free water, measured on the same day.

The constants were now applied to the measurement of the viscosity of two substances by two different observers (Table IV). The viscosity

TABLE III. *Values of m_l and m_r of viscometer 1−31.*

Substance	Temp. °C	m_l	m_r
Water	20.00	1.49	0.64
Water	20.00	1.49	0.63
Water	20.00	1.48	0.80
Water	20.00	1.49	0.86
Water	20.00	1.64	0.64
Water	20.00	1.58	0.64
Water	20.00	1.19	0.67
Water	20.00	1.30	0.55
o-Chlorotoluene	100.00	1.50	0.74
m-Chlorotoluene	100.00	1.47	0.78
p-Chlorotoluene	100.00	1.47	0.77
o-Bromotoluene	100.00	1.48	0.75
m-Bromotoluene	100.00	1.47	0.77
p-Bromotoluene	100.00	1.46	0.78
o-Nitrotoluene	100.00	1.52	0.69
m-Nitrotoluene	100.00	1.40	0.84
o-Phenetidine	100.00	1.34	0.90
m-Phenetidine	100.00	1.44	0.78
		Average 1.46	0.74

TABLE IV. *Comparison of deviations of right and left limb determinations by using (A) $h_1 = +0.25$, and $m_l = m_r = 1.12$, and (B) $h_1 = +0.01$, $m_l = 1.46$ and $m_r = 0.74$.*

Temp.°C	p (app.) (cm)	(in cp)	A(%)	B(%)
I. p-Chlorotoluene			*Observer, Geddes*	
10.00	203.5*	1.0325	−0.10	0.10
20.00	149.6	0.8926	−0.09	−0.03
30.00	149.8*	0.7844	−0.20	−0.01
40.00	100.4	0.6976	−0.04	−0.09
60.00	100.5*	0.5643	−0.20	−0.02
80.00	77.9	0.4686	−0.09	0.00
100.00	77.9	0.3975	−0.32	+0.05
		Average	0.15	0.04
II. Triethyl amine			*Observer, Brown*	
0.00	106.8*	0.4656	−0.43	0.00
10.00	84.8	0.4122	−0.17	+0.19
20.00	84.8	0.3685	−0.71	−0.19
30.00	84.8*	0.3316	−0.88	−0.15
40.00	68.9	0.2999	−0.50	+0.07
60.00	57.4	0.2491	−0.68	+0.04
80.00	57.0	0.2108	−1.18	0.00
		Average	0.65	0.09

* Note that for these values, just before the pressure was lowered and hence the flow rapid, the differences in column A are greatest.

given is the average for the two limbs, but in column A the calculations have been made with $m_l = m_r = 1.12$ and $h_1 = 0.25$ cm, while in column B it has been assumed that $m_l = 1.46$ and $m_r = 0.74$ and $h_1 = 0.01$ cm. It is to be noted that when the flow takes place in both directions there is a marked improvement of the concordance by the use of the two different values of m. Furthermore the difference in column A, as may be observed in the starred values of Table IV, is greatest just before the pressure was lowered because of the flow becoming too rapid. It is to be understood that viscosities would not be in error in any case if values were always the average of determinations in both directions, but if single determinations were depended upon they might be appreciably in error.

The authors then examined data by previous workers to see whether the opportunity for a correction here noted could be readily detected. If an author did not measure the flow in both directions, it was not possible to detect the error involved, but wherever the data were sufficiently complete the value of this correction appeared to be demonstrable. Even the important data of Thorpe and Rodger[6] may be used to demonstrate the value of the correction, although in their study they used but two pressures (not widely different) approximately 100 and 130 g/cm². Space is not available for reproducing these tables which have been worked out. This work suggests that when one plans to measure viscosity with the flow in one direction only, it is of importance to give particular attention to the measurement of m.

[6] Thorpe and Rodger, Phil. Trans. **A185**, 397 (1894).

The Fluidities and Associations of Alcohols and Esters of High Molecular Weight

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The specific volumes and fluidities of six isomeric hexadecyl alcohols and the corresponding hexadecyl acetates have been measured from 0 to 100°C where practicable. The associations of these liquids have been calculated and shown to be extraordinarily low. This suggests the importance of further studies on the association of compounds of high molecular weight and low association.

INTRODUCTION

THE association of liquids as determined by the fluidity method[1] is taken as the ratio of the temperature required to give a certain fluidity to the temperature calculated from atomic constants. These constants are derived from compounds which are assumed to be non-associated. The values of the association are relative until it can be proven that the compounds used as a basis for comparison are unassociated. Because of the work of Darrall[2] and of Fornwalt,[3] the search for non-associated substances does not need to be haphazard. It is necessary to avoid associating groups or else to provide protection for them. Protection is, for example, afforded by long or numerous aliphatic residues surrounding the associating group.

TABLE I. *A summary of the fluidities and specific volumes of all the alcohols.*

Temp.	ϕ	V	Temp.	ϕ	V
2 Ethyl tetradecanol			*2 Propyl tridecanol*		
20	2.628	1.1898	20	2.792	1.1927
30	4.322	1.1996	30	4.574	1.2018
40	6.707	1.2092	40	7.109	1.2115
60	14.23	1.2300	60	15.22	1.2331
80	26.39	1.2516	80	28.25	1.2544
100	43.68	1.2741	100	46.32	1.2766
2 Butyl dodecanol			*2 Amyl undecanol*		
20	2.469	1.1934	20	2.539	1.1932
30	4.100	1.2027	30	4.177	1.2038
40	6.452	1.2128	40	6.569	1.2141
60	14.21	1.2339	60	14.37	1.2344
80	26.98	1.2550	80	27.07	1.2554
100	45.50	1.2776	100	46.17	1.2780
2 Hexyl decanol			*2 Heptyl nonanol*		
20	2.413	1.1944	20	2.453	1.1939
30	3.978	1.2040	30	4.040	1.2035
40	6.308	1.2139	40	6.360	1.2130
60	13.95	1.2349	60	13.99	1.2342
80	26.81	1.2568	80	27.01	1.2561
100	45.80	1.2790	100	46.04	1.2789

[1] Bingham and Miss Harrison, Zeits. f. physik. Chemie **66**, 1 (1909).

[2] Bingham and Darrall, J. Rheology **1**, 174 (1930).

[3] Bingham and Fornwalt, J. Rheology **1**, 372 (1930).

TABLE II. *A summary of the fluidities and specific volumes of all the acetic esters.*

Temp.	ϕ	V	Temp.	ϕ	V
Hexadecyl acetate			*2 Methyl pentadecyl acetate*		
20	12.81	1.1616	0	6.381	1.1482
30	17.05	1.1715	10	9.569	1.1581
40	22.30	1.1814	20	13.50	1.1683
60	34.46	1.2032	30	18.21	1.1782
80	49.01	1.2245	40	23.69	1.1884
100	68.10	1.2464	60	36.82	1.2103
			80	52.62	1.2322
			100	70.52	1.2504
2 Ethyl tetradecyl acetate			*2 Propyl tridecyl acetate*		
0	6.620	1.1403	0	6.305	1.1421
10	9.275	1.1501	10	9.687	1.1525
20	13.36	1.1602	20	13.97	1.1625
30	18.11	1.1700	30	19.18	1.1724
40	23.75	1.1803	40	25.24	1.1828
60	37.32	1.2008	60	39.86	1.2041
80	53.65	1.2229	80	57.44	1.2256
100	72.29	1.2480	100	77.06	1.2476
2 Butyl dodecyl acetate			*2 Amyl undecyl acetate*		
0	6.020	1.1426	0	6.040	1.1443
10	9.394	1.1520	10	9.376	1.1534
20	13.65	1.1677	20	13.64	1.1633
30	18.88	1.1744	30	18.89	1.1736
40	24.47	1.1824	40	25.03	1.1846
60	39.76	1.2042	60	39.79	1.2053
80	57.77	1.2269	80	57.63	1.2271
100	78.26	1.2489	100	78.53	1.2497
2 Hexyl decyl acetate			*2 Heptyl nonyl acetate*		
0	6.099	1.1435	0	6.034	1.1428
10	9.485	1.1535	10	9.373	1.1525
20	13.84	1.1635	20	13.65	1.1625
30	19.15	1.1735	30	18.89	1.1731
40	25.43	1.1843	40	25.06	1.1832
60	40.59	1.2053	60	40.00	1.2052
80	59.10	1.2276	80	58.35	1.2266
100	80.66	1.2497	100	79.47	1.2493

Materials

The materials used in this study were six isomeric hexadecyl alcohols and the corresponding hexadecyl acetates made by Mr. Warren Cox at Johns Hopkins University in cooperation with Dr. E. Emmet Reid. No further purification was undertaken than to afford foreign particles an opportunity to settle.

The liquids were measured at 0, 10, 20, 30, 40, 60, 80, and 100°C where practicable. Several of the samples were solid to above 10°C.

The results obtained for the alcohols are summarized in Table I and for the esters in Table II. Summaries of the two sets of tables are given in Table III and IV.

TABLE III. *The association* of the hexadecyl alcohols.*

Substance	Assoc. (n) $\phi = 10$ rhes	Assoc. (n) $\phi = 50$ rhes
2 Ethyl tetradecanol	1.274	1.102
2 Propyl tridecanol	1.267	1.094
2 Butyl dodecanol	1.274	1.096
2 Amyl undecanol	1.274	1.093
2 Hexyl decanol	1.275	1.094
2 Heptyl nonanol	1.275	1.094

TABLE IV. *The association of the hexadecyl acetic esters.**

Substance	Assoc. (n) $\phi = 10$ rhes	Assoc. (n) $\phi = 50$ rhes	Assoc. (n) $\phi = 100$ rhes
Hexadecyl acetate	0.991	0.914	0.884
2 Methyl pentadecyl acetate	0.991	0.902	0.888
2 Ethyl tetradecyl acetate	0.992	0.900	0.885
2 Propyl tridecyl acetate	0.989	0.889	0.874
2 Butyl dodecyl acetate	0.991	0.889	0.871
2 Amyl undecyl acetate	0.991	0.889	0.869
2 Hexyl decyl acetate	0.991	0.889	0.864
2 Heptyl nonyl acetate	0.991	0.889	0.867

* Atomic temperature constants of Bingham and Spooner.

Discussion of Results

The fluidities of the isomeric alcohols are so nearly the same that only the two most divergent members are shown in Fig. 1. The same statement may be made in regard to the esters. The esters, however, are more fluid because of lower association.

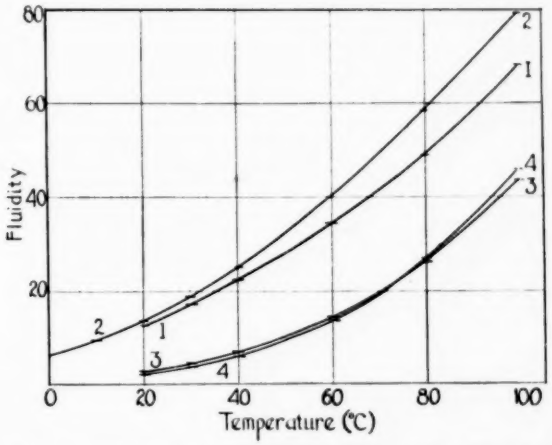

FIG. 1. Fluidity-temperature curves. (1) 2-hexadecyl acetate, (2) 2-heptyl nonyl acetate, (3) 2-ethyl tetradecanol, (4) 2-heptyl nonanol.

The specific volumes of the alcohols differ only slightly: 0.39 percent at 20° and 0.38 percent at 100°. Among the esters the difference in specific volume is also small: 0.70 percent at 0°C and 0.32 percent at 100°C. All the alcohols have a positive association as expected, and it is appreciably higher at a fluidity of 10 rhes than at 50 rhes. The esters, however, have uniformly an association which is less than unity. This signifies that these esters may be employed to determine the atomic fluidity constants. This conclusion confirms the one reached by DeTurck[4] by an entirely different method. Such compounds should however be studied at temperatures above 100°C in order to obtain fluidities of the greatest interest.

[4] Bingham and DeTurck, J. Rheology **3**, 479 (1932).

The Viscosity of Barium Chloride in Aqueous Solution

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Measurements are made on the viscosity of aqueous solutions of barium chloride at 18°C over the range 0.006 to 0.492 molality. The value of the constant A in the equation $\eta=\eta_c/\eta_0=1+Ac^{\frac{1}{2}}$ is determined and found to agree, within 4 percent, with the theoretical value of the constant as determined by Falkenhagen and Vernon. The constants of several empirical equations are also given.

INTRODUCTION

IN the course of some investigations in progress in this laboratory we found occasion to measure the viscosities of dilute aqueous solutions of $BaCl_2$ at 18°C. The relative viscosity of aqueous $BaCl_2$ at 25°C has been precisely measured by Jones and Dole,[1] who found the relative fluidity $\varphi=\varphi_c/\varphi_0$ to be related to the square root of the concentration, c (in mols per liter):

$$\varphi=1-0.02013c^{\frac{1}{2}}-0.20087c.$$

Since the effect of interionic forces in opposing the motions of ions in an electric field has been shown to be proportional to the square root of the concentration in very dilute solutions, this work suggested the development of a formula for the evaluation, from electrostatic theory, of the constant A in the equation $\eta=\eta_c/\eta_0=1+Ac^{\frac{1}{2}}$. Falkenhagen and Dole[2] developed the special case of uniunivalent electrolytes, and Falkenhagen and Vernon[3] have worked out the general relation for the evaluation of this constant of viscosity as applied to any electrolyte solution. Experimental verification of the Falkenhagen-Dole function for uniunivalent electrolytes has been obtained in several recent investigations[4] as well as by the interpretation of some earlier measurements.[5]

Our data will serve to test the more general equation developed by Falkenhagen and Vernon as applied to electrolytes of the diunivalent type.

EXPERIMENTAL

Apparatus

The viscometer has been previously described.[6] The instrument is capable of measurement of relative viscosity with an experimental error not exceeding 1 part in 10,000 but much practice is needful in attaining this precision, just as it is in other skills which depend upon exact coordination of hand and eye.

Materials

The $BaCl_2$ used was "Baker's Analyzed," recrystallized, and air dried. Solutions were made up by weight in conductivity water. The concentration of the most concentrated solution was checked by gravimetric precipitation of AgCl; dilute solutions were made by weighing in additional water to a weighed portion of a more concentrated one. Molal concentrations were converted into molar concentrations by the use of the densities (given in Table I) interpolated from the *International Critical Tables*.

Data

The experimental results are summarized in Table I.

[1] Jones and Dole, J. Am. Chem. Soc. **51**, 2950 (1929).

[2] Falkenhagen and Dole, Zeits. f. physik. Chemie **B6**, 159 (1929); Phys. Zeits. **30**, 611 (1929); Falkenhagen, Phys. Zeits. **32**, 745 (1931).

[3] Falkenhagen and Vernon, Phys. Zeits. **33**, 140 (1932).

[4] Joy and Wolfenden, Nature **126**, 994 (1930); Smith, Wolfenden and Hartley, J. Chem. Soc. **1931**, 403; Joy and Wolfenden, Proc. Roy. Soc. (London) **A134**, 413 (1931); Hood, J. Rheology **3**, 326 (1932); Jones and Talley, privately communicated by Grinnell Jones.

[5] Grüneisen, Wiss. Abh. Phys. Reichanstalt **4**, 151, 237 (1905), cited from Jones and Dole[1]; Applebey, J. Chem. Soc. **97**, 2000 (1910); Merton, J. Chem. Soc. **97**, 2454 (1910).

[6] Hood, J. Rheology **3**, 326 (1932).

TABLE I. *Viscosity of barium chloride at 18°C.*

Solution Runs	A 4	B 4	C 4	D 4	E 4	F 2
Molality (m)	0.4921	0.1132	0.05686	0.02504	0.01221	0.00581
Density	1.0842	1.0180	1.0080	1.0032	1.0010	1.0000
Molarity (c)	0.4751	0.1121	0.05653	0.02497	0.01219	0.00580
$\eta=\eta_c/\eta_0$	1.1211	1.0240	1.0134	1.0061	1.0034	1.0020
$(\eta-1)/c$	0.255	0.214	0.237	0.244	0.279	0.345
$\varphi=\varphi_c/\varphi_0$	0.89195	0.97656	0.98682	0.99394	0.99668	0.99800
$c^{\frac{1}{2}}$	0.6893	0.3349	0.2378	0.1580	0.1104	0.0762
$(\varphi-1)/c^{\frac{1}{2}}$	−0.1568	−0.0700	−0.0554	−0.0384	−0.0301	−0.0262
$(\varphi-1)/c^{\frac{1}{2}}$ calculated by Eq. (1)	−0.1564	−0.0722	−0.0532	−0.0389	−0.0309	−0.0254
$\Delta(\varphi-1)/c^{\frac{1}{2}}$ Obs.—Calc.	−0.0004	0.0022	−0.0022	0.0005	0.0008	−0.0008
φ by Eq. (1)	0.89218	0.97581	0.98735	0.99383	0.99659	0.99806
$\Delta\varphi_1$	−0.00023	0.00075	−0.00052	0.00011	0.00009	−0.00006
φ by Eq. (2)	0.89217	0.97601	0.98731	0.99374	0.99650	0.99801
$\Delta\varphi_2$	−0.00022	0.00055	−0.00049	0.00020	0.00018	−0.00001

INTERPRETATION OF RESULTS

When the values of $(\eta-1)/c$ were plotted as ordinates against the corresponding values of c as abscissas, a curve was obtained which exhibited a minimum between 0.2 and 0.3 molar. The initial downward slope of the curve corresponds to a negative curvature in the viscosity-concentration curve; and the minimum to a point of inflection in the latter. Comparison with the data of Jones and Dole[1] showed that the negative curvature is more pronounced at the lower temperature; in accord with the finding of Applebey.[5]

When the values of $(\varphi-1)/c^{\frac{1}{2}}$ were plotted against $c^{\frac{1}{2}}$ on a large scale for the graphical estimation of the constant A in the Falkenhagen-Dole function

$$\eta=1+Ac^{\frac{1}{2}}+\cdots$$

the linear relationship found by Jones and Dole

$$(\varphi-1)/c^{\frac{1}{2}}=-A-Bc^{\frac{1}{2}}$$

at 25°C was not obtained; instead, the points located a curve (Fig. 1) of slight but definite curvature.

A smooth curve was drawn through the points and the intercept on the $(\varphi-1)/c^{\frac{1}{2}}$ axis determined. This gave $A=0.014$.

As the curve was *nearly* linear, it was assumed that it could be fitted to an equation of the form $y=A+Bx+Cx^2$. Three ordinates were read off the curve at round values of $c^{\frac{1}{2}}$, and used to establish the constants A, B, C. The derived equation was

$$(\varphi-1)/c^{\frac{1}{2}}=-0.0140-0.143c^{\frac{1}{2}}-0.0923c. \quad (1)$$

Comparisons between the values of $(\varphi-1)/c^{\frac{1}{2}}$ and φ computed by Eq. (1) and the observed values are given in Table I. It is seen that the equation defines the values of φ throughout the course of the curve with an accuracy of 1 part in 3000 without systematic trend.

Since equal errors in the measurement of η have a greater effect in defining the equation of the curve relating $(\varphi-1)/c^{\frac{1}{2}}$ and $c^{\frac{1}{2}}$ at small values of c than at larger values; we assumed as an empirical equation connecting φ and c

$$\varphi=1-Ac^{\frac{1}{2}}+Bc+Cc^2+Dc^3+\cdots,$$

dropping terms of higher order than c^2. Analysis of the data by the use of tabular differences gave as the equation

$$\varphi=1-0.0137c^{\frac{1}{2}}-0.1616c-0.0958c^2. \quad (2)$$

Comparison between the values of φ computed by Eq. (2) and the observed values is given in

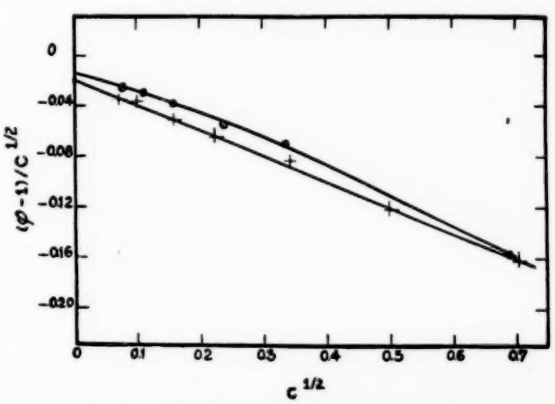

FIG. 1. The Falkenhagen-Dole function for $BaCl_2$ at 18°C. The lower curve (crosses) is that for 25°C after Jones and Dole.

Table I. The sum of the squares of the residuals is somewhat smaller for Eq. (2) than for Eq. (1), but the deviations of the two curves are scarcely significant except in the evaluation of the constant A.

The value of A computed by the equation of Falkenhagen and Vernon from the ionic mobilities of the ions Ba^{++} and Cl^{-} is $A=0.0145$. Found: by graph, 0.014; by Eq. (1), 0.0140; by Eq. (2), 0.0137.

It is significant that the value of B is by both equations smaller than that found by Jones and Dole.[1] When the Falkenhagen-Dole function is plotted as in Fig. 1, not only $BaCl_2$ but also such uniunivalent electrolytes as have been measured at two or more temperatures offer visible evidence that the value of B is conditioned not only by the type of solute (e.g., at 18°C. B is *positive* for $RbNO_3$ and *negative* for HNO_3) but also by the temperature. If it is postulated that the fluidity of an aqueous solution of strong electrolyte is governed by the law of additive fluidities, plus a stiffening effect due to interionic attraction tending to decrease the fluidity, plus a depolymerization of complex $(H_2O)_x$ molecules tending to increase the fluidity; then for a given solute at a given concentration, $\eta=\eta_c/\eta_0$ must be greater at the higher temperature, for at the higher temperature there will be fewer $(H_2O)_x$ molecules in equilibrium with (H_2O) molecules in the pure solvent, and the dissociation effected by each molecule of added electrolyte must be correspondingly less as the number of $(H_2O)_x$ molecules within its sphere of influence diminishes; while at low temperatures and low concentrations the change in the ratio of partial molal volumes will be negligible over temperature intervals markedly affecting the ratio of $(H_2O)_x$ to (H_2O); whence *the decrease in the initial slope* of the curve

$$(\varphi-1)/c^{\frac{1}{2}}=-A+Bc^{\frac{1}{2}}+\cdots$$

with increase in temperature.

The Viscosity of Urea in Aqueous Solution

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(Received March 9, 1933)

While examining the literature relating to the viscosity of aqueous solutions, the writer noticed some measurements obtained in connection with the viscosity of aqueous urea which appeared to warrant a reinvestigation of this substance. The relative viscosity of aqueous urea was accordingly measured at 18°C and 25°C over a range of concentration from 0.005 to 1.876 mol/liter. Fluidity—volume-concentration curves exhibit negative curvature, evidencing that urea behaves like an electrolyte in that it decreases the fluidity of water less than would be expected on the basis of additive fluidities. It behaves like a non-electrolyte in that it exhibits no stiffening effect; i.e., the value of the Falkenhagen constant A is zero. A table is included, giving a comparison of the observed and calculated values of the Falkenhagen constant A for 11 electrolytes.

THE viscosity of aqueous electrolyte solutions is occupying considerable attention at the present time. Recent investigations have shown that the equations of Arrhenius,[1] Einstein,[2] and Herz,[3] are equally unsatisfactory in expressing the relation between the viscosity and the concentration of such solutions. The equation

$$\eta_c/\eta_0 = 1 + Ac^{\frac{1}{2}} + Bc + \cdots \qquad (1)$$

put forward empirically by Jones and Dole[4] has obtained theoretical confirmation from considerations of the Debye-Hückel theory. Falkenhagen and Dole[5] have evaluated the constant A for the special case of binary electrolytes with ions of equal mobilities, and Falkenhagen and Vernon[6] have developed a general equation evaluating this constant for *any* electrolyte.

Theoretically, the value of A must be positive for electrolytes, and zero for non-electrolytes. Experimental verification of the equation is given in Table I.

While examining the literature relating to the viscosity of solutions, I recently noticed some measurements obtained in connection with the viscosity of aqueous urea which appeared of sufficient interest to warrant a reinvestigation of this substance.

TABLE I. *Comparison of theoretical and experimental values of A in Eq. (1).*

Electrolyte	Temp.	A (Theory)	A (Found)	Reference
KCl	18°	0.0049	0.0052	7, 12
KCl	25°	0.0050	0.0052	13
KCl	35°	0.0052	0.0051	12
$KClO_3$	18°	0.0051	0.0028	8
$KClO_3$	18°	0.0051	0.0050	12
$KClO_3$	25°	0.0054	0.0050	13
$KClO_3$	35°	0.0058	0.0049	12
$KBrO_3$	25°	0.0058	0.0058	13
$LiNO_3$	18°	0.0069	0.0082	9
KNO_3	25°	0.0052	0.0050	13
$RbNO_3$	18°	0.0049	0.0070	10
$RbNO_3$	18°	0.0049	0.0050	12
$RbNO_3$	25°	0.0051	0.0040	10
$RbNO_3$	35°	0.0054	0.0056	12
$CsNO_3$	18°	0.0048	0.0103	11
$CsNO_3$	25°	0.0050	0.0043	13
HNO_3	18°	0.0021	0.0021	12
HNO_3	35°	0.0025	0.0023	12
$LiIO_3$	18°	0.0094	0.0108	14
NH_4Cl	25°	0.0050	0.0057	13
$BaCl_2$	25°	0.0147	0.0201	4

Solutions of urea, as measured roughly by Rudorf[15] at 25°C show that a small concentration of urea decreases the viscosity of water. Fawsitt,[16]

[1] Arrhenius, Zeits. f. physik. Chemie **1**, 285 (1888).
[2] Einstein, Ann. d. Physik **19**, 289 (1906).
[3] Herz, Zeits. f. anorg. Chemie **99**, 132 (1917).
[4] Jones and Dole, J. Am. Chem. Soc. **51**, 2950 (1929).
[5] Falkenhagen and Dole, Phys. Zeits. **30**, 611 (1929); Falkenhagen, Phys. Zeits. **32**, 365 (1931).
[6] Privately communicated by E. L. Vernon, publication forthcoming. Cf. Phil. Mag. [7] **14**, 537 (1932).
[7] Joy and Wolfenden, Nature **126**, 994 (1930).
[8] Hood, J. Rheology **3**, 326 (1932).
[9] Applebey, J. Chem. Soc. **97**, 2000 (1910).
[10] Smith, Wolfenden and Hartley, J. Chem. Soc. **1931**, 403.
[11] Merton, J. Chem. Soc. **97**, 2454 (1910).
[12] Joy and Wolfenden, Proc. Roy. Soc. **A824**, 413 (1931).
[13] Jones and Talley, J. Am. Chem. Soc. **55**, 624 (1933).
[14] Grüneisen, quoted from reference 4.
[15] Rudorf, Zeits. f. physik. Chemie **43**, 257 (1903).
[16] Fawsitt, Proc. Roy. Soc. Edin. **25**, 51 (1904).

investigating the physico-chemical properties of the amides, reexamined the viscosity of aqueous urea at 25°, finding his results in accord with the Arrhenius equation. His data show no "negative viscosity." Ranken and Taylor,[17] measuring the viscosity of dilute solutions at six temperatures over the range 8° to 45°, found their results to confirm those of Fawsitt in that they were unable to obtain any evidence of negative viscosity at 25°; at 8°, however, they observed the phenomenon: at 0.03125 mol per liter $\eta_c/\eta_0 = 0.9985$.

Dunstan and Mussell,[18] have also measured the viscosity of urea solutions over a wide range of concentration at 25°. While their viscosity curve offers no direct evidence of negative viscosity, it was observed when their data were plotted in the form $(\eta_c/\eta_0-1)/c^{\frac{1}{2}}$ *versus* $c^{\frac{1}{2}}$ a curve was obtained which (with slight extrapolation) indicated that the quantity $(\eta_c/\eta_0-1)/c^{\frac{1}{2}}$ must be negative at the limit $c=0$. Solutions of non-electrolytes which exhibit negative viscosity are extremely rare, although non-aqueous systems have been reported where the phenomenon is apparently established.[19] The measurements of Fawsitt[16] and of Ranken and Taylor[17] appeared to leave no ground for the idea that aqueous urea exhibits this phenomenon at 25°. Again, assuming as a first approximation the Arrhenius equation applied by Fawsitt, $\eta_c/\eta_0 = K^c$, this transforms into $\eta_c/\eta_0 = 1+\beta c+\beta^2c^2/2!+\beta^3c^3/3!+\cdots$ (where $\beta = \ln K$) and since K is nearly unity, β is small, so that for small values of c, $\eta_c/\eta_0 = 1+\beta c$, whence $(\eta_c/\eta_0-1)/c^{\frac{1}{2}} = \beta c^{\frac{1}{2}}$, which must pass through the origin.

Since the extrapolation involved in the graphical analysis of the data of Dunstan and Mussell was inconsiderable, it was concluded that the negative intercept obtained might be due to an inflection in the curve arising from a dissociation of water effected by the solute.

The characteristic properties of water were explained thirty years ago by Sutherland[20] on the basis of its molecular constitution as a system

$$(H_2O)_3\left\{\begin{array}{c}\rightleftharpoons\\ \rightleftharpoons H_2O\rightleftharpoons\end{array}\right\}(H_2O)_2$$

and he suggested that "the viscosity of aqueous solutions must be highly complicated on account of the action of the solute in altering the proportions of dihydrol and trihydrol in the solution . . . the solute converts enough of the viscous trihydrol into the less viscous dihydrol to more than compensate for the increase of viscosity which its own presence imparts."[20]

The works of Bingham and his associates[21, 22, 23, 24] and of Sheppard and Houck[25] support the hypothesis that liquid water consists chiefly of associated molecules, and establish association as an important factor in determining the fluidity of liquids.

In view of the possible value of the data in formulating the trend of dissociation of the solvent with change in concentration, it was thought worth while to examine the course of the viscosity—concentration curve for aqueous urea at high dilution, extending the measurements over a range of concentration sufficient to allow comparison with the results of Dunstan and Mussell.

Experimental

Apparatus

The viscometer has been previously described.[8] The probable error of a determination of relative viscosity as the average of a pair of observations (from 5 determinations of the viscosity of water at 18° involving 13 observations) attainable with the instrument is by the method of least squares 0.008 percent.

Materials

The urea used was "Merck's Technical," purified by repeated crystallizations, first from water and then from ethyl alcohol and dried at 60°. The purified material melted sharply at 133°

[17] Ranken and Taylor, Trans. Roy. Soc. Edin. **45**, 397 (1906).

[18] Dunstan and Mussell, J. Chem. Soc. **97**, 1935 (1910).

[19] Wagner and Mühlenbein, Zeits. f. physik. Chemie **46**, 867 (1903).

[20] Sutherland, Phil. Mag. [5] **50**, 460 (1900).

[21] Bingham, Hyden and Hood, Ind. Eng. Chem. **16**, 25 (1924).

[22] Bingham and Darrall, J. Rheology **1**, 174 (1930).

[23] Bingham and Fornwalt, J. Rheology **1**, 372 (1930).

[24] Bingham and Spooner, J. Rheology **3**, 221 (1932).

[25] Sheppard and Houck, J. Rheology **1**, 349 (1930).

TABLE II. *Viscosity of urea.*

Series	m	c mols/liter	ρ	$\bar{v}_2$	V Vol. %	η_c/η_0	$(\eta-1)/c$	φ_c/φ_0	φ rhes
				25°C					
A	2.0530	1.8759	1.0264	44.89	8.420	1.08698	0.0475	0.91998	102.941
E	1.5837	1.4776	1.0217	44.75	6.612	1.06500	0.044	0.93897	105.065
B	0.9802	0.93645	1.0116	44.52	4.169	1.03915	0.042	0.96232	107.678
A_1	0.5549	0.5399	1.0054	44.43	2.399	1.02089	0.039	0.97953	109.604
E_1	0.3817	0.3742	1.0028	44.36	1.660	1.01400	0.037	0.98619	110.350
A_2	0.1004	0.09964	0.9984	44.26	0.441	1.00400	0.040	0.99602	111.449
B_1	0.05014	0.049875	0.9977	44.24	0.221	1.00193	0.039	0.99807	111.678
B_2	0.02003	0.01995	0.9973	44.23	0.088	1.00072	0.036	0.99928	111.814
B_3	0.01001	0.00998	0.99715	44.22	0.044	1.00040	0.040	0.99960	111.850
B_4	0.00500	0.00498	0.9971	44.22	0.022	1.00020	0.040	0.99980	111.872
				18°C					
A		1.8789	1.0280		8.433	1.07948	0.042	0.92638	87.734
E		1.4799	1.0233		6.622	1.05943	0.040	0.94390	89.393
B		0.9379	1.0132		4.176	1.03535	0.038	0.96586	91.473
A_1		0.5408	1.0070		2.403	1.01972	0.0365	0.98066	92.874
E_1		0.3748	1.0044		1.663	1.01270	0.034	0.98746	93.518
A_2		0.09980	1.0000		0.442	1.00375	0.038	0.99626	94.352
B_1		0.04996	0.9993		0.221	1.00168	0.034	0.99832	94.547
B_2		0.01998	0.9989		0.088	1.00066	0.033	0.99934	94.644
B_3		0.00999	0.99875		0.044	1.00036	0.036	0.99964	94.672
B_4		0.00499	0.9987		0.022	1.00020	0.040	0.99980	94.687

(uncorrected). Water was redistilled. Solutions were made up by weight, the dilute solutions being made by weighing in additional water to a weighed portion of a more concentrated one.

Stability of solutions

According to Lewis and Burrows[26] equilibrium in the reaction

$$CO(NH_2)_2+2H_2O\rightleftharpoons(NH_4)_2CO_3$$

is not established in 95 days at 77°C; while Walker and Hambly[27] find that equilibrium in the reaction

$$CO(NH_2)_2.Aq\rightleftharpoons NH_4CNO$$

is not attained at 100°C in the course of 2 hours. Therefore, at room temperatures the solutions should be practically stable. Three original solutions were made up during the course of the measurements: these are indicated in the tabulated data by the letters A, B, E, with the dilutions made from them marked by appropriate subscripts. The measurements on each series were completed within 11 days after the original solution was made up.

A sample of solution B_2, $m=0.02003$, $\eta_c/\eta_0=1.00066$ at 18°, sealed in an ampule and heated to 100° for 220 minutes then gave $\eta_c/\eta_0=1.00113$, from which it appears that as the solutions age the viscosity will increase, and hence the negative curvature found cannot be attributed to the chemical instability of the solute.

Density

Densities of solutions were calculated by the formulas

$$\rho(25°)=0.9970+0.01453m-0.000426m^2$$

(where m is the molality) derived from data of Dunstan and Mussell at 25°, and

$$\rho(18°)=0.9986+0.01453m-0.000426m^2,$$

based upon the constancy of the partial molal volume of urea; an assumption which seems justified by the values of $\bar{v}_2$ at 25°.

Data

The experimental results are summarized in Table II.

INTERPRETATION OF RESULTS

Column 8 of Table II shows that at low concentration the quantity $(\eta-1)/c$ is approximately constant, evidencing a linear relationship between η and c. The equations

$$\eta(18°)=1+0.036c,$$

$$\eta(25°)=1+0.039c$$

[26] Lewis and Burrows, J. Am. Chem. Soc. **34**, 1515 (1912).
[27] Walker and Hambly, J. Chem. Soc. **67**, 746 (1895).

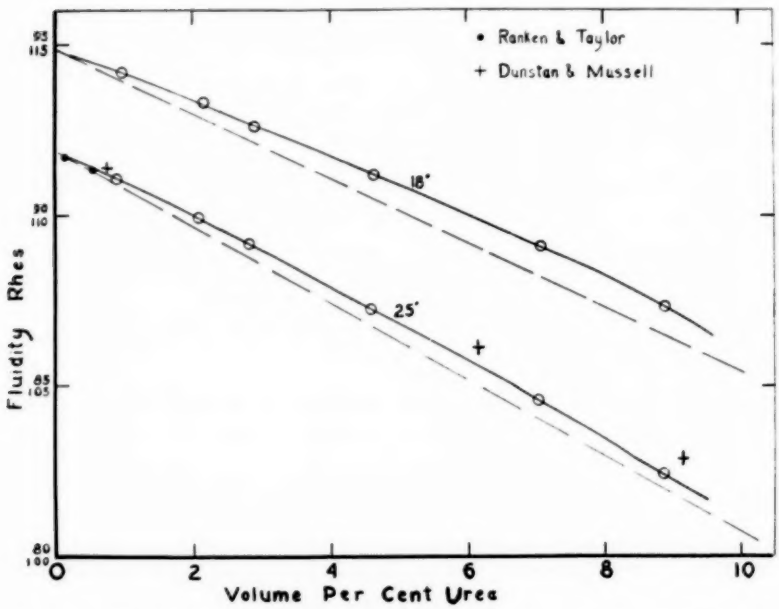

FIG. 1. Fluidity of urea as function of volume percent. Deviation from the theoretical law of additive fluidities is shown.

express the viscosity at low concentration. At higher concentrations the viscosity increases more rapidly.

When $(\eta-1)/c^{\frac{1}{2}}$ was plotted against $c^{\frac{1}{2}}$, inflected curves were obtained which passed through the origin; the points of inflection appearing at about 0.25 molar. Likewise when $(\eta-1)/c$ was plotted against c, the points appeared to locate sagged curves with the minima at about the same concentration. Attempts to find a simple relation expressing the viscosity as a function of concentration failed, although nearly linear relations were obtained when the fluidity was plotted against either the molality or the volume percent of solute. The deviation from the theoretical law of additive fluidities is shown in Fig. 1. The measurements of Ranken and Taylor and 3 measurements of Dunstan and Mussell are plotted for comparison at 25°.

The relations

$$\varphi(18°)=1-0.03586m \text{ and } \varphi(25°)=1-0.03897m$$

represent the observed fluidities with an accuracy of 0.1 percent; these equations expressing the chords connecting the ordinates at the abscissas $m=0$, $m=2.053$, of the curves in question.

From these considerations it is concluded that urea behaves in aqueous solution as a non-electrolyte in that it exhibits no stiffening effect; i.e., the value of the constant A in the Falkenhagen equation is zero. It behaves like an electrolyte in that it decreases the fluidity of water less than would be expected on the basis of additive fluidities, and also (apparently) exhibits a point of inflection in its $\eta-c$ curve at moderate concentration (about 0.25 molar) which accords with Applebey's suggestion[9] that when a salt is dissolved in water there are two opposed effects, one of which is a depolymerization of complex water molecules tending to diminish the viscosity.*

* Subsequent to the submission of this paper, Jones and Talley[13] have reported experimentally established values of the Falkenhagen constant A, which have been included in a revision of Table I. These authors also record the Falkenhagen constant for urea: $A=0$; and find that the viscosity of aqueous urea at 25°C is expressed over the range of concentration 0.002 to 0.2 *molar* by the relation

$$\eta_c/\eta_0=1+0.03784c$$

The Automatic Timing of the Ostwald Viscometer by Means of a Photoelectric Cell

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(Received December 27, 1932)

A new method for the automatic measurement of the time of flow of a liquid in a viscometer of the Ostwald type by means of a photoelectric cell is described. The elimination of the psychological errors inherent in the older technique permits greater precision. Other sources of error in the use of the Ostwald viscometer are analyzed and the precautions necessary for precision viscometry are discussed.

AS the result of the work of many investigators beginning with Poiseuille,[1] it is well known that some salts give aqueous solutions which have a viscosity greater than that of pure water at the same temperature, whereas other salts give solutions which are less viscous than water if the temperature and concentration are not too high.

Sprung,[2] Arrhenius[3] and others have shown that the viscosity-concentration curves are nearly linear but have a positive curvature at high concentrations.

In 1905 Grüneisen[4] demonstrated experimentally that at low concentrations the viscosity-concentration curves, instead of becoming more nearly linear, actually develop a negative curvature. He was, however, unsuccessful in his attempts to account theoretically for this effect.

In 1923, Debye and Hückel suggested that the weakness of the classical theory of electrolytic dissociation of Arrhenius was the neglect of the electric forces between the ions. They pointed out that the mutual attractions and repulsions of the ions would tend to establish and maintain a preferred arrangement of the ions which may be crudely described as a space lattice, and that these forces would resist a disturbance of this preferred arrangement. Debye and Hückel, and Onsager have discussed in detail the case of a disturbance due to the presence of charged electrodes within the solution and have derived an equation for the variation of electric conductance with the concentration. In 1929, Grinnell Jones and Malcolm Dole[5] applied this theory for the first time to the problem of the viscosity of solutions. They pointed out that the flow of a solution in a capillary tube would disturb the ionic lattice and therefore the electric forces would measureably increase the viscosity and inferred that this effect would be proportional to the square root of the concentration. Since the viscosity-concentration curves are approximately linear it is evident that there are one or more other effects of the dissolved salt which are proportional to the concentration. Jones and Dole proposed the equation

$$1/\eta = \varphi = 1 - Ac^{\frac{1}{2}} \pm Bc$$

and showed that this equation is in harmony with the best available data. They also predicted that all strong electrolytes would give solutions having a viscosity greater than that of pure water at the same temperature if measured at sufficiently low concentrations, even including those salts which cause a decrease in viscosity at moderate concentrations.[6]

The primary purpose of this investigation was to develop a sufficiently precise method for the measurement of the viscosity of dilute solutions to be able to test the validity of the Jones and Dole equation and of their prediction that at

[1] J. L. M. Poiseuille, Ann. chim. phys. [3] **21**, 76 (1847).
[2] A. Sprung, Ann. d. Physik **159**, 1 (1876).
[3] S. Arrhenius, Zeits. f. physik. Chemie **1**, 285 (1887).
[4] E. Grüneisen, Wiss. Abb. Phys. Techn. Reichsanstalt **4**, 151, 237 (1905).
[5] Grinnell Jones and Malcolm Dole, J. Am. Chem. Soc. **51**, 2950 (1929).
[6] For a more detailed account of the historical and theoretical background of the present investigation see Grinnell Jones and S. K. Talley, J. Am. Chem. Soc. **55**, 624 (1933).

great dilution all salts increase the viscosity of water. Since for these purposes a high precision must be attained, we set as our goal the determination of the viscosities of dilute aqueous solutions relative to that of water at the same temperature with an error of not more than one part in ten thousand. We decided that the method of timing the flow of a definite volume through a capillary tube in a modified form of Ostwald viscometer was the most suitable method for our purpose but that a much better method of timing would have to be invented to eliminate the psychological error inherent in the older technique. We needed some automatic device which would record the interval between the time of passage of the meniscus past the upper and lower marks on the volume measuring bulb of the viscometer with a precision substantially greater than is attainable with a manually operated stopwatch. We succeeded in creating an effective mechanism by which the meniscus transit in the capillary tube of the viscometer operates the recording pen of a chronograph. This new method of timing a viscometer gave promise of attaining a precision of the order of 0.01 second.

We then designed a new viscometer of the Ostwald type modified to adapt it to the new method of timing and of such dimensions that the period when filled with water at 25°C would be about 10 minutes. Our new instrument, which is shown in Fig. 1, was built of quartz at the Lynn Works of the General Electric Company.

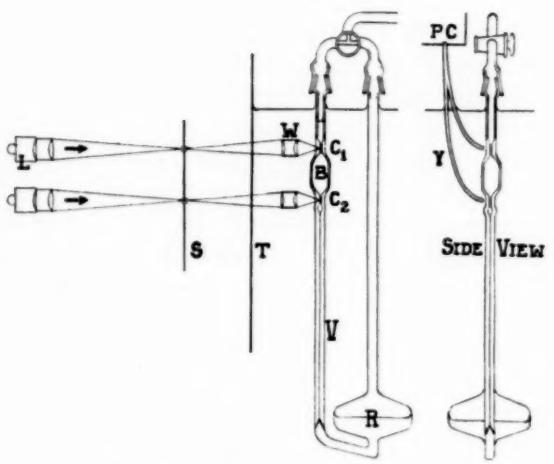

FIG. 1. Viscometer and optical system.

It had approximately the following constants: average hydrostatic head, 21.5 cm; volume of the upper bulb, 10.063 ml; internal diameter of the upper bulb, 1.8 cm; the length of the capillary, 18.5 cm; the diameter of the capillary 0.0476 cm; internal diameter of the lower bulb, 6.8 cm; period with water at 25°C, 618 seconds.

The improvement in the timing made it necessary to refine some other details of the design and manipulation in an effort to ensure that none of the other sources of error would individually cause an error in the final result which would be greater than that due to an error of 0.01 second in the timing.

An error in the final results may be due to any of the following causes: (a) an error in timing, (b) irregular drainage, (c) a variation in the average or effective hydrostatic head, (d) an error in the computation of the kinetic energy correction, (e) contamination of the viscometer and solutions, (f) an error in the determination of the concentration, (g) an error in the determination of the effective densities of the solutions, (h) inadequate control of the temperature.

Each of these sources of error will be discussed below with an explanation of the modifications of the usual design and of the experimental precautions which we have found to be necessary or helpful. Special emphasis will be placed on the new method of timing because of its novelty and because it controlled many of the features of the design and manipulation.

The following possible sources of error were considered and found to be negligible for our instrument in dilute solutions (at least up to 0.1 *N*): (a) the back pressure due to the shearing along the Helmholtz double layer, (b) the heating of the working liquid by viscous friction in passing through the capillary, (c) the back pressure caused by the viscous resistance of the air in the connecting arm and upper constriction, (d) the variations of pressure caused by differences in surface tension of water and the solution.

A. A New Timing Device for Viscometers Capable of a Precision of 0.01 Second

When a vertical capillary tube of about one millimeter bore is filled with water or an aqueous

solution and strongly illuminated by a horizontal beam of light focussed on the bore, most of the light continues across the tube with only a slight deflection as shown in Fig. 2. But when the meniscus drops below the illuminated portion of the tube so that the light meets a water-air interface, a part of the light is deflected aside at about right angles to the original path of the beam, as is shown in Fig. 3. This effect is due to

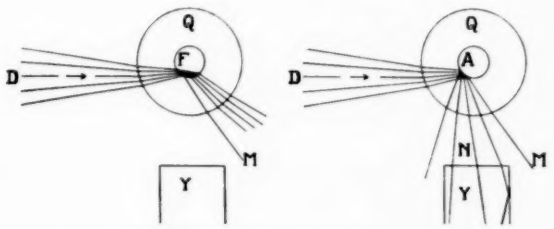

FIG. 2. FIG. 3.
Principle of optical effect at meniscus transit.

total internal reflection of the light at that portion of the newly formed inner cylindrical water-air interface where the angle of incidence of the light exceeds the critical angle.

The light thus reflected to one side may be made to enter and activate a photoelectric cell and thus give a weak electric impulse at the instant of the passage of the meniscus past the illuminated part of the tube. This primary electric impulse may then be strengthened by a suitably designed audion tube amplifier so that it is powerful enough to operate the recording pen of a chronograph.

The new method of observing the passage of the meniscus in the capillary constriction of the viscometer requires a bright beam of light which is narrow vertically and wide enough horizontally to illuminate at least half of the width of the capillary. This beam must be focussed on the capillary of the viscometer at a definite reproducible height. The source of the light was an automobile lamp (Mazda No. 81, 6 candle power, 6 volts) with a straight tungsten filament which was mounted so that the filament would be horizontal. In order to secure more intense illumination the lamp was operated with 10 volts instead of its rated 6 volts.

A two lens optical system was adopted because of its extreme flexibility, ease of adjustment, permanence when adjusted, and general dependability. It consists of one primary condensing-projecting lens, L, and two final lenses, w, as shown in Fig. 1. The lamp and first lens are contained in one unit mounted in a box. The box is set in an elevator and can be raised and lowered so the beam of light is projected through the glass wall of the thermostat, T, upon one or the other of the two final lenses. The two positions of the box in the elevator corresponding to the setting for the two final lenses are fixed by stops. (In the figure this part of the optical system is drawn in duplicate merely for the sake of clarity.) The projected beam is brought to a focus just before the thermostat at which point a screen, s, is set up. Two horizontal slits are cut in the screen corresponding to the size and shape of the image of the filament of the bulb at the two positions set by stops on the elevator. The screen cuts out stray light from the first lens and makes it possible to replace a burned-out bulb without altering the position of the filament, because the position of the lamp can be adjusted until the focussed image is in the slit. In actual operation the replacement of one bulb by another, even during a run, did not alter the time of flow by more than 0.01 second.

The two final lenses, called "water lenses," were supported in the thermostat in a manner which permitted them to be adjusted until the light was properly focussed and then they were firmly and permanently clamped in a definite position with reference to the viscometer. They each are composed of two glass lenses which, with their mountings, form water-tight cells having the more refractive surfaces of the lenses in contact with the air enclosed in the cell. The lenses were cemented into place by sealing and baking them with pure, solvent-free Canada balsam. Such an arrangement obtains the greatest relative aperture of the lens with the least aberration. The same arrangement also makes it possible to have a lens system with the same focal length whether submerged in water or not. The final lenses act as fulcrums to the beam of light and, by analogy with the lever, it can be seen that the displacement of the final image on the constriction of the viscometer will be only a small fraction of the displacement of the primary focus at the screen. The ratio is 1 to 7 in the apparatus as set up.

The projection-condensing lens is a Bausch and Lomb series II Cinephor with an effective focal length of 5 inches and a relative aperture of 3.5. The two water lenses were made by the firm of Pinkham and Smith of Boston through the kindness of Mr. J. A. Seaverns. They have an effective focal length of 75 millimeters and a relative aperture of 2.5.

It was the usual practice to have the lamp lit for only a few seconds at each transit to conserve the lamp. In some special experiments the lamp was lit and focussed on the lower constriction immediately after the upper transit to determine whether the heating effect of the lamp on the liquid would be great enough to influence the time of flow. The results indicated that any possible heating effect was entirely negligible. This gratifying result is not surprising since the heat rays are absorbed by the water of the thermostat and the quartz is so transparent that little light is converted into heat at the viscometer.

The next problem was the mounting of the photoelectric cell so as to receive the light deflected to the side at the two constrictions of the viscometer when the meniscus passes. The viscometer must of course be immersed in a water thermostat, but there are great difficulties in immersing a photoelectric cell under water. It would have to be placed in a box which is absolutely water-tight in order to secure adequate electric insulation. A properly diaphragmed window for the light to enter would be necessary. An amplifier is necessary to increase the photoelectric current to a usable value. If the amplifier were put in the same box with the cell, the mechanical difficulties would increase. The box would require more electrical leads and the heat of the amplier would tend to prevent the adequate control of the temperature of the thermostat. If the amplifier were not in the same box, the situation would be worse. The long electrical leads from the cell are very sensitive to stray electric fields and the whole recording apparatus would be rendered unstable. There is the added difficulty that there are two meniscus transits to record requiring that the photoelectric cell and amplifier be duplicated in whole or in part or that it be made movable.

Happily the junior author had an inspiration which led to a satisfactory solution of this difficult situation. In air, a fused quartz rod has the property of carrying light through its length in almost undiminished intensity, even around bends, by virtue of total internal reflection and a low coefficient of absorption. Quartz will serve the same purpose when immersed in water with the qualification that the higher index of refraction of water requires that the bends in the rod may not be as sharp as in air. By this device the light could be carried from the viscometer to the photoelectric cell which was placed outside the thermostat in a dry, light-tight, electrically shielded box. The amplifier was also contained in the same box.

In the final form of the apparatus, the quartz rods for carrying the light to the photoelectric cell were made in the form of a Y. The two rods, one for each constriction, were fused together into one which carried the light to the photoelectric cell. The "quartz Y," whose form and placement is indicated in Fig. 1, is rigidly clamped to the permanent viscometer mounting in the thermostat. The use of the quartz rods has the further advantage that only the light falling on the ends has any effect; each end acts as a small diaphragmed window. The fusion of the two rods into one fixes the measured volume of efflux to some extent because an equal vertical displacement of both will leave the volume unchanged.

The photoelectric cell used was obtained from the General Electric Company and was designated by them as type PJ 23. It proved to be more sensitive than several other makes which were tried. The original cell has been used thousands of times and is still apparently as good as new. The voltage applied to the cell is indicated in Fig. 4.

The current from the photoelectric cell is of the order of microamperes and must be amplified before it can be used to operate a chronograph. The photoelectric current increases with the increasing of the light in the quartz rod and was shown, by oscillographic tests kindly conducted by Dr. R. F. Field and Mr. H. W. Lamson of the General Radio Company of Cambridge, to take 0.05 second to attain to a maximum. This corresponds to a frequency of 5 cycles per second. The amplifier used is shown diagrammatically in

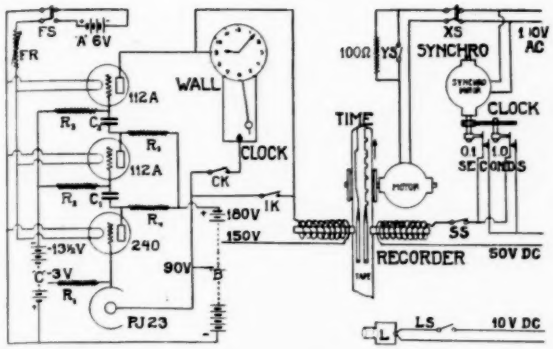

FIG. 4. Photoelectric cell, amplifier and electrical connections.

Fig. 4. It contains three audion tubes with resistance-capacitance coupling. Care was taken to keep the inductance at a minimum to make the time lag of the response negligible. The types of tubes and the voltages used are indicated in the diagram. The capacities C_1 and C_2 are each 2 microfarads and the resistances R_1, R_2, R_3, R_4 and R_5 are, in order, 20, 2, 1, 2, and 1 megohms. The best values of the last four depend to some extent on the particular tubes. A change in the "A" voltage from 5 to 6 volts causes a variation of less than 0.001 percent in the recorded time.

The output current to the chronograph has a constant "background" value of 2 milliamperes which rises, when activated by the meniscus transit, to over 20 milliamperes. The spring tensions on the armatures of the recording pens were adjusted to respond only to currents greater than 5 milliamperes.

The increased current output of the first tube of the amplifier continues as long as the increased light from the quartz Y falls on the photoelectric cell but, because of the nature of the coupling between the tubes, the duration of the increased current through the chronograph depends upon the amplifier constants. By using the stated values of the resistances and capacities, the duration of the deflection of the chronograph pen, arising from a meniscus transit, is about two or three seconds. The extended character of the transit record distinguishes it from the other records of the same pen.

It is to be noted that successive stages are out of phase by 180 degrees so that, if the chronograph is to be operated on the increase of current, there must be an odd number of stages in the amplifier.

The oscillographic measurements referred to above showed that it takes 0.05 second for the current to build up to its maximum. This probably means that it takes 0.05 second for the meniscus to pass through the illuminated portion of the constriction. But this does not mean that there is an uncertainty of 0.05 second in our final result. The recording pen responds to some definite value of the increasing current less than the maximum, and will therefore record the same stage of the transit at the upper and lower constriction; consequently the interval will be correct. Reducing the intensity of illumination by lowering the voltage by a third may produce an increase of the recorded time as great as 0.028 second.

We depended on an eight-day weight-driven pendulum clock for our standard of time. The pendulum of Invar was fitted with a platinum tip which gave an electric impulse every second by making contact with mercury at the bottom of every swing. The clock was not checked for variations in rate over small time intervals but it showed adequate constancy over periods of months. The equality of alternate seconds was checked to 0.001 second at frequent intervals. The clock was assembled by the Gaertner Scientific Company of Chicago and is described in their catalogue under the number L 1013.

Our procedure of determining the water value every day makes our observations independent of a changing clock rate over long periods of time. Variations during the course of a day may be safely disregarded because of the uniform conditions of the room in which the clock is kept. To test the effect of temperature, the clock was electrically heated to 45°C and tests were made with the use of the viscometer as a standard. No appreciable variation was observed.

Changing the size of the mercury drop, through which the tip of the pendulum must swing, from the smallest to the largest stable size altered the rate of the clock by 0.035 second in 618. Because the size of the drop remains constant for months at a time, the likelihood of an appreciable error from this source is entirely negligible.

A synchronous electric clock, whose rate depends on the frequency of alternation of our 60 cycle electric power, was fitted with contactors for tenths of seconds and for full seconds and its record was used to divide the full seconds record from the standard clock. This synchro-clock is standard equipment made by the General Radio Company under their type number 511S. This clock proved to be unreliable as a primary standard of time because the frequency of our electric supply is not maintained sufficiently constant at the power house. But for the purpose of subdividing the seconds given by the pendulum clock it is only necessary that the rate of the electric clock shall not vary more than 1 percent within the second of the transit. This modest requirement seems to be met adequately.

The chronograph used in this investigation was a Duplex Syphon Pen Recorder made by the General Radio Company and designated as Type 456. As its name implies, it is fitted with two syphon pens controlled by independent electromagnets. The record is made on ordinary stock market ticker tape which moves at the rate of 30 centimeters per second when records are being made. One pen is used for recording the meniscus transit, the full seconds from the standard clock and also the manually impressed identification marks from key *IK*, Fig. 4. The other pen merely records the seconds and tenths of seconds from the synchro-clock. All times are read in terms of the arbitrary units of the synchro-clock time and are corrected therefrom to the standard time.

Since we have records on the tape every tenth of a second, a variation in the speed of motion of the tape could not influence our results by 0.01 second unless the speed varied by 10 percent within the critical tenth second. Since the tape is always started a few seconds before the transit there is no danger of an acceleration of this magnitude at the transit.

Tests made during the noon hour, when the fluctuations of the city current are greatest, indicated that the use of the synchronous clock did not cause an error greater than 0.003 second.

The recording devices are operated only at the times of transit as indicated in the following procedure:

The liquid is drawn up in the left arm of the viscometer to definite mark, about 2 cm above the upper constriction, C_1, by sucking through a rubber tube attached to the free end of the Pyrex cross piece. The level of the liquid is held there by closing the three-way stopcock when the air pressure has been decreased in the left arm of the viscometer, by sucking, to just the proper amount to hold the level stationary. The high dilution of all the solutions measured in this investigation renders quite negligible any evaporation that might be caused to take place by the application of suction to the surface of the solution in the above operation.

Calculations indicated and experiments confirmed that very vigorous raising of the liquid in the preparation for a measurement, could cause an increase in temperature of as much as 0.007°C. Consequently, only gentle suction was applied and the liquid, after being drawn up above C_1, was allowed to remain there approximately a minute and a half. It was found experimentally that self-consistent results could be thereby obtained.

Twenty seconds before the meniscus transit is to be measured, the photoelectric cell and amplifier are turned on by throwing in the switch *FS*, Fig. 4. Ten seconds later, the pens of the recorder are lowered onto the tape and the tape started moving at slow speed by switch *XS*. The switch, *SS*, connecting the synchro-clock to the recorder is thrown in at the same time. Immediately afterwards the three-way stopcock is turned to connect the two arms of the viscometer with each other and with the atmosphere. The operator then takes his seat before the thermostat, throwing in the switch, *LS*, which controls the lamp that illuminates the constriction of the viscometer and observes the fall of the liquid in the viscometer. When it lacks 4 or 5 seconds of the transit, he presses the key, *IK*, momentarily and thereby identifies one of the full seconds as registered on the face of the synchro-clock. (The hour, minute and second of this identification are held in mind until the operations listed in this paragraph are complete, and then recorded in the laboratory notebook.) Immediately afterwards, he throws the switch, *YS*, shorting the resistance in series with the recorder motor and thereby brings the recording tape to recording speed. At the same time, he

presses the key, *CK*, that records the full seconds impulses from the standard clock. Within a fifth to a half second before the transit, he releases the key, *CK*, in order that the standard clock seconds shall not interfere with the actual transit record if it should happen to coincide. Within 1 to 2 seconds after the transit, he opens the filament switch, *FS*, of the amplifier, timing the action to correspond to a full second indicated on the face of the synchro-clock. This last action identifies another full second; if the current impulse from the photoelectric action is still continuing, it stops; if it has ceased, a current surge will make a mark similar to the first identification mark. The light switch, *LS*, and the recorder switch, *XS*, and the time impulse switch, *SS*, are opened in succession and the pens of the recorder are raised. The identified seconds are all recorded in the laboratory notebook.

The same operation is repeated for the lower transit, taking due care also to turn on the photoelectric cell amplifier twenty seconds before the transit. The average of three consecutive runs whose extreme values do not differ by more than 0.02 second is generally taken as the time of efflux of a given solution although a limit of 0.03 is sometimes accepted.

B. Drainage

In order that the drainage should be as perfect as possible the tube *B* was ground and polished internally to remove any imperfections in the surface before being drawn down and sealed to the constrictions. The glass blower was instructed to make the segments of the bulb connecting the wide part of the bulb to the constrictions as nearly true cones as possible in order that the slope would be steep at all points.

The constancy of transpiration times is an assurance that the amount of liquid left on the walls of the volume bulb is constant for a given solution. If the volume of undrained liquid retained on the walls of the upper bulb at the instant of the meniscus transit is appreciably different for water and for the solutions this will make an error in the measurement. Since our bulb was designed to favor the drainage and the time of flow was long in our instrument we have assumed that this effect is negligible for the dilute solutions so far investigated. The possibility of error from this source in work with concentrated solutions needs careful study.

The constrictions C_1 and C_2 were made longer than usual to facilitate the method of timing described above. In order that the events being timed should be as nearly identical as possible the constrictions were cut from the same piece of tubing.

We have built a second viscometer in which the internal diameters of the two constrictions were so proportioned that the linear velocities of the meniscus in the two constrictions were approximately the same. We have not yet decided which is the better design.

The internal diameter of this tube is an important detail. By making this tube narrow the linear rate of motion of the meniscus is increased and therefore the event being timed is made more definite. But if the constriction is made too narrow, the liquid draining down from the wet walls above will form a drop which bridges across the constriction and obstructs the free flow of the air which follows the meniscus. This obstruction will be broken by the suction of the receding liquid but capillarity will draw the drop back into the constriction and the obstruction will be reformed and broken repeatedly. The true net or effective hydrostatic pressure is thus altered by a pulsating and erratic back pressure so that precise results cannot be obtained under these conditions. The tendency to form drops in the constriction depends on many factors including the surface tension of the liquid, its viscosity, the rate of flow, the area and slope of the drainage surface and the diameter of the constriction. These factors, except the diameter of the constriction, are either uncontrollable or are determined by other considerations, and hence place a lower limit to the diameter of the constriction. Special experiments showed that under our conditions the best diameter for the upper constriction was 0.10 cm which was therefore specified.

C. Control of the Hydrostatic Head

In determining relative viscosities with the Ostwald viscometer, the exact value of the effective hydrostatic head need not be known. It is important only that it be kept constant, or

if it is not kept constant, that due allowance be made for variations. Our viscometer had an average hydrostatic head of 21.5 centimeters and a transpiration time for water at 25°C of 618 seconds. Consequently, a variation of the effective head of only 0.000,35 cm would alter the time by 0.01 second. An inspection of the instrument shows that the hydrostatic head can be varied both by alteration in the mounting and by changes of the total volume of liquid added to the viscometer for a measurement.

The mounting was so designed as to give a definite and reproducible setting of the viscometer and yet permit the ready removal of the instrument from the thermostat for cleaning and drying. To this end, the viscometer was permanently mounted in a stout frame of angle brass and always handled in this movable frame. During measurements the movable frame was held in the thermostat by a three point support on a rigid permanent structure which was built of angle brass, and provided with cross braces designed to have mechanical stability and give a minimum of interference with the proper circulation of the water in the thermostat.

The contact points between the two frames, one at the bottom and one at the top of each side, were made of Monel metal because this metal is hard and does not corrode. The bottom contact consisted of a rounded cone pointing upward, attached to the permanent frame; and a corresponding true cone or cup with a slightly greater angle of flare recessed into the movable frame. This lower contact supported the weight of the viscometer. The two upper contacts merely helped to fix the position of the viscometer. The upper left contact consisted of a rounded cone, with a horizontal axis and attached to the permanent frame, and corresponding to it on the movable frame, a groove into which it fitted. The plane sides of the groove had a slightly greater angle of flare than the cone. The axis of the groove was directed toward the bottom contact. The upper right contact consisted of a hemisphere on the permanent frame and a plane surface on the movable frame. A spring clamp, working on a hinge and bearing on a plane surface on the movable frame in line with the two upper contacts, locked the viscometer in place. If all the contacts are of the cup and cone type, there is strong probability that they will defeat the purpose of a three point suspension unless they are very precisely matched. The position of the lower contact of the viscometer was fixed in three dimensions, the upper left in two and the upper right contact in one. The possibility of one contact point conflicting with the functions of another is absolutely eliminated by the arrangement described above.

In order to test the reproducibility of the mounting, several runs were made on the times of transit of a fixed quantity of water in the viscometer. Between each run the viscometer and movable frame were removed and replaced on the Monel metal supports. No other changes were made. The following results were obtained: 618.462, 618.457, 618.462, 618.462, 618.459 seconds.

A maximum variation of only 0.005 second for five successive runs which extended over a period of seven hours demonstrates that the timing mechanism, the mounting, and the constancy of the thermostat are adequate.

A feature in the design of the viscometer that happily was not required in this research was the placing of a drainage sump under the lower reservoir, *R*, as indicated in Fig. 1. By the use of this sump all liquids could be removed by sucking through a glass tube inserted down the open arm. This feature was added because we were not sure when the viscometer was built that the mounting would be sufficiently reproducible. We therefore planned, if necessary, to clean and dry it without disturbing the mounting.

The total amount of liquid added to the viscometer in successive fillings was not held perfectly constant but variations were measured and allowed for. The lower reservoir, *R*, has a diameter of 6.8 centimeters and a variation of 0.013 milliliter of water changed the time of flow by 0.01 second; a calculation that was verified by experiment. It is impractical to have a lower reservoir of much greater diameter. The liquid to be measured was delivered to the open arm of the viscometer from a special weight pipette which was designed to deliver as definite a volume as possible each time, and yet permit the actual volume delivered to be determined by weighing the pipette to milligrams before and after emptying the pipette. The delivery tube of

the pipette was brought up in form of a goose neck to a level with the upper tube. If the volume actually delivered differed from the standard working volume (about 60 ml) by a significant amount a correction to the time was applied. These corrections averaged less than 0.01 second.

D. The Kinetic Energy Correction

The kinetic energy correction must be applied in work of high precision, best by the method suggested by Bingham.[7] However there is some uncertainty in two of the factors used in the computation of this correction, namely the value of the coefficient, m, and the length of a capillary which has flared ends. We have thought it best to decrease the magnitude of the correction and hence minimize the error in computing it by using a narrow (0.0476 cm) and long (18.5 cm) capillary thus giving a long period (about 618 seconds). With this instrument the correction on the relative viscosity was never more than 0.00020 for any salt which we have investigated up to 0.1 N and therefore the error in estimating the correction can hardly exceed the limit which we have set as our goal. For concentrated solutions this question is more serious and may require additional precautions. Lengthening the period by any means except increasing the measured volume tends to decrease the correction. Our viscometer was substantially better in this respect than the instrument used by Jones and Dole. This matter was an important consideration in the design of our instrument.

E. Contamination of the Viscometer and Solution

Precision viscometry requires exceptional pains to secure and maintain absolute cleanliness. Occasionally grossly erratic results are obtained which can only be ascribed to minute particles of dust becoming lodged in the capillary or to traces of grease. Reducing the diameter of the capillary, which is advantageous in other respects, increases this difficulty markedly. We have found that the fraction of the experiments which have to be rejected because the results are obviously erratic can be reduced by extreme care to ensure cleanliness.

[7] E. C. Bingham, *Fluidity and Plasticity*, pp. 18, 75. McGraw-Hill Book Company, New York, 1922.

We have found it necessary to filter everything that goes into the viscometer—water, solution, cleansing agents, and air. We have used either sintered glass filters of Pyrex or a small platinum sponge made like a Gooch-Neubauer crucible.

Traces of grease are ruinous. No liquid should ever be put into the viscometer unless it will drain perfectly on the walls of its container. We have found a hot mixture of strong sulfuric acid and nitric acid the best cleaning agent. After using this mixture the instrument must be thoroughly washed with distilled water. We have found it much more difficult to wash out a sulfuric acid-chromic acid cleansing agent, especially from the filters.

F. The Determination of the Concentration

Solutions below 0.2 molal were, in general, made up volumetrically. A weighed quantity of dried salt was dissolved and made up to volume, due care being taken to allow for any departure from the standard temperature of 25°. All the more concentrated solutions were made up by completely gravimetric procedures and especial care was taken to avoid concentration by evaporation.

For dilute solutions the requirements for precision in making up the solutions are not very severe. Thus, for example, for caesium nitrate at 25°C the following equation holds

$$\eta = 1 + 0.00486c^{\frac{1}{2}} - 0.09569c;$$

hence

$$\partial\eta/\partial c = +0.00243/c^{\frac{1}{2}} - 0.09569$$

if $c = 0.1N$, $\partial\eta/\partial c = -0.088$.

Therefore if the concentration is known within 0.0002 mole per liter, or 0.2 percent of its value, the corresponding error in the relative viscosity will be only 0.0000176 which corresponds to an error of about 0.01 second in the timing. Most salts have less steep viscosity-concentration curves than caesium nitrate at low concentrations so that the requirements are less severe. These requirements are usually easily met provided the salt can be dried without decomposition.

On the other hand, for concentrated solutions (1 N and above) extreme care may be necessary in the preparation of the solutions and in their

handling to prevent a change in concentration due to evaporation.

If the error in determining the concentration is due to an impurity in the salt being weighed, it makes a difference whether the impurity is water or a saline impurity. A saline impurity which increases the viscosity will be especially objectionable in a salt which decreases the viscosity and *vice versa*.

G. Density

Density enters into the calculations as a direct factor and must be measured with the same precision as the desired viscosity. In practice, it is a very simple matter to determine density with a precision greater than 0.001 percent and it became the rule in our routine to determine the density of every solution measured. For this purpose Pyrex pycnometers of the Ostwald type were used. They had a capacity of 50 milliliters and glass capped ends.

There is a very important point to be considered in regard to the use of densities. It is not the true density that creates the hydrostatic pressure in the viscometer but that density less the density of the air. Since this buoyant action of air is so well understood in its application to weighing, it is enough to point out that this effect can become appreciable. In the case of 1 N KBr, for example, the error introduced by using true vacuum densities instead of apparent densities in air is -0.01 percent. The changes in air density during the course of a day rarely, if ever, cause an appreciable error.

H. Control of the Temperature

The temperature coefficient of the viscosity of water is approximately 2 percent per degree at 25°C. Therefore a variation of 0.0008°C in the average temperature of the viscometer during a measurement would correspond to an error of 0.01 second in the timing. The consistency of our results indicates that this requirement was met adequately. This good performance was secured by the use of a large thermostat, with an exceptionally large and sensitive regulator, vigorous stirring, a heater with a small heat capacity, large radiating surface and suitable power, and a device to maintain a constant level. But since none of these means is novel they need not be described in greater detail.

Conclusion

The new viscometric procedures described above have proved adequate for the purposes for which they were developed. We have used this new method of timing for the measurement of the viscosities of dilute solutions of six salts and two non-electrolytes but refrain from giving the results here because they have recently been published in full elsewhere.[6] It is planned to continue the work in this laboratory by measurement on other salts and at other temperatures and in other solvents. The amount of precise data needed for a survey of this field is so extensive that we hope that others will share in the labors of its collection in order to speed the day when the general laws of the viscosities of solutions will be definitely established. Our experience shows that the new method of timing permits greater precision by eliminating the psychological error which is inherent in the older technique and is sufficiently practical to warrant its more extended use in other laboratories.

The Plastic Properties of Several Types of Unvulcanized Rubber Stocks at High Rates of Shear

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An extrusion plastometer operating at rates of shear comparable with those existing in rubber tubing machines (10 to 1000 sec.$^{-1}$) is described. The relation between efflux rate and pressure at constant temperature for various types of rubber stocks was determined. For highly compounded rubber stocks, such as tread stocks, the efflux rate *vs.* pressure curves attain linearity at low rates of shear. Both the slope of the curves and the extrapolated pressure intercept vary rapidly with the temperature, indicating that both the mobility and the yield stress are functions of temperature for highly compounded stocks. For lightly compounded stocks and for crude rubber, the curves are of the power function type at the lower rates of shear, but appear to attain linearity at the very high rates. These linear portions of the curves, for a given stock at different temperatures, are approximately parallel. Elastic recovery was determined as a function of rate of efflux. The slope of the recovery *vs.* efflux rate curves decreases with increasing rates of efflux. The relation between efflux rate at constant temperature and pressure, and time of milling, is approximately linear. The extrusion plastometer is shown to be more sensitive to overmilling than is the Williams plastometer. The partial failure of the compression-type plastometer to correlate with the factory extrusion machine is explained on the basis of the much lower rates of shear employed in the compression-type instrument than those existing in the extrusion machine.

INTRODUCTION

MARZETTI,[1, 2, 3] Griffiths[4] and others[5, 6, 7] have employed the extrusion method for studying the plastic properties of unvulcanized rubber. Some of the results, particularly those of Marzetti, have been very interesting from an academic standpoint. However, none of these experimenters has employed rates of shear differing greatly from those of the compression-type plastometers,[8, 9, 10] which operate at rates much lower than those existing in factory tubing machines. It seemed, then, that this fact might explain why no great discrepancies between extrusion plasticity results and those of the parallel-plate compression-type plastometer were found, at least insofar as could be discovered in the literature. Hence, it was thought desirable, from both an academic and a practical standpoint, to make a study of the flow of rubber through an orifice over a wide range of rates of shear.

RATE OF SHEAR AS A CRITERION OF FLOW CONDITIONS

In order that a testing instrument may correlate with factory processes, it is obvious that the flow conditions in the testing instrument should be made to coincide with those in the factory machines. This raises the question as to what physical entity completely describes the flow conditions at a given temperature, either in a factory machine or in a measuring instrument. Two physical quantities are available for use in such a description, the shearing stress F_s and the rate of shear dv/dx where v is the velocity of the plastic material at a distance x from the axis of a capillary through which the material is flowing under a pressure P. If R be the radius of the capillary and L its length, the shearing stress at the walls is:

$$[F_s]_R = PR/2L. \qquad (1)$$

The equation relating dv/dx with F_s is sometimes assumed to be

[1] B. Marzetti, India Rubber World **68**, 776 (1923).
[2] B. Marzetti, Rubber Age (London) **6**, 139 (1925–26).
[3] B. Marzetti, Rubber Age (N. Y.) **15**, 454 (1924).
[4] R. W. Griffiths, Trans. Inst. Rubber Ind. **1**, 308 (1925–26).
[5] J. Behre, Kautschuk **8**, 2 (1932).
[6] F. Elliott, Trans. Inst. Rubber Ind. **3**, 468 (1927–28).
[7] G. Martin, Trans. Inst. Rubber Ind. **6**, 298 (1930).
[8] Van Rossem and Van der Meijden, Rubber Chem. Tech. **1**, 393 (1928).
[9] E. Karrer, Ind. Eng. Chem. **21**, 770 (1929).
[10] Williams, Ind. Eng. Chem. **16**, 362 (1924).

$$dv/dx = ((F_s - f)/c)^n, \qquad (2)$$

where f is the yield stress; c the consistency; and n a constant for a given material. For $n=1, f=0$, (2) becomes the equation of viscous flow in a perfect liquid. For f finite, $n=1$, (2) becomes the equation of a truly "plastic" material, as defined by Bingham.[11]

The use of the shearing stress F_s as a criterion of flow conditions is forbidden because, in tubing machines, the pressure is, in general, unknown. Hence, we must rely on the rate of shear dv/dx as a criterion of flow conditions. This is apparently a rather logical quantity to use in this connection, for it always has the form of a linear velocity of extrusion divided by the cross-sectional dimension of the orifice. These two major variables determine the rate of extrusion at a given pressure and temperature. Obviously the dependence of dv/dx upon the coordinates makes it necessary to employ some sort of averaging process, in order to give a quantity which can be calculated for different orifices and different rates of flow. Consequently a rather arbitrary method of averaging has been employed, namely that of volume weighting. By definition, then, the mean rate of shear is:

$$(dv/dx)_{ave} = \int_0^h (dv/dx) A_1^1(x, t)dx / \int_0^h A(x, t)dx, \qquad (3)$$

where v is the linear velocity of extrusion; x the coordinate normal to flow with origin at the center of the orifice. $A(x, t)dx$ is the volume element under the steady state velocity front, in which the rate of shear has a value dv/dx; t is the time, and h the semi-cross-sectional dimension of the orifice. Another assumption must be made in order to compute this integral, i.e., the form of the velocity front. Inasmuch as the velocity front for the case ($n=1$, $f \ll F_s$) in Eq. (2) is of substantially parabolic section, it seemed that the assumption of a parabolic section for the general case would not introduce great error into the result. Furthermore, since we are interested chiefly in the relative rates of shear, and the only deviations caused by error in the selection of the type of velocity front are small changes in the constant q in the relation

$$(dv/dx)_{ave} = q v_{ave}/D, \qquad (4)$$

where v_{ave} is the mean velocity of extrusion, and D the cross-sectional dimension, there is no necessity for extreme accuracy in our geometrical assumption.

The calculation of the integral (3) is a perfectly straightforward process and yields the results:

$$-(dv/dx)_{ave} = 9v_{ave}/4D \qquad (5)[12]$$

for a rectangular slit orifice of infinite length, and

$$-(dv/dx)_{ave} = 64v_{ave}/15D \qquad (6)[12]$$

for a circular orifice.

The relation (5) is directly applicable to the compression type of plastometer. For example, in the Williams plastometer, the flow may be considered as extrusion through a rectangular slit of continuously decreasing width and increasing length. Then, assuming constant volume and Williams' equation

$$yt^n = K, \qquad (7)$$

the mean rate of shear at the periphery of the pellet can be shown to be

$$(dv/dy)_{ave} = (9n/8)(V/\pi)^{\frac{1}{2}}(1/K^5)\cdot y^{\frac{1}{2}} \qquad (8)$$

at a given distance of separation of the plates y and where V is the volume of the pellet.

For the Goodrich type of parallel plate plastometer, in which the plates have the same area as the ends of the cylindrical pellet, similar considerations, including Taylor's equation[8]

$$1/y^2 - 1/y_0^2 = kt, \qquad (9)$$

where y is the separation of plates at time t, y_0 the original separation of plates at $t=0$, and k a constant, yield

[11] E. C. Bingham, *Fluidity and Plasticity*, 1922.

[12] The validity of formulas (5) and (6) has been partially verified by an experiment to be described in a subsequent paper. Efflux rates of tube stock from a slit orifice and a circular orifice mounted in a single extrusion machine were measured simultaneously, i.e., at the same temperature and pressure. Assuming a linear relationship between rate of shear and shearing stress, it was found that the mean rates of shear, as computed for the orifices by (5) and (6) respectively, agreed within 30 percent, after the proper correction for the fact that the shearing stresses in the two orifices were different, had been applied. Thus, the formulas (5) and (6) give at least the order of magnitude of the relative mean rates of shear for the slit orifice and circular orifice, respectively.

$$(dv/dy)_{ave} = 9Rk/16[1/(kt+1/y_0^2)^{\frac{1}{2}}], \quad (10)$$

where R is the radius of the plates.

Table I gives the numerical values of $(dv/dx)_{ave}$ as computed from the formulas (5), (6), (9) and (10). The values are the maxima for each of the instruments, respectively, except for the authors' plastometer, which can attain a rate of shear somewhat over 1000/sec. with a moderate sacrifice in the accuracy of measurement of the extrusion velocity. The values given for the two types of tubing machines are thought to be typical.

TABLE I. *Numerical values of mean rates of shear for various instruments and machines.*

Experimenter	Type of instrument	Formulae used	$\left(\frac{dv}{dx}\right)_{ave}$	Remarks
Griffiths[4]	Extrusion plastometer	(6)	58.5/sec.	Size of die uncertain, piston type.
Behre[5]	Extrusion plastometer	(6)	1.28/sec.	Air pressure type.
Marzetti[3]	Extrusion plastometer	(6)	1.38/sec.	Air pressure type.
Elliot[6]	Extrusion plastometer	(6)	0.54/sec.	Piston type.
Martin[7]	Extrusion plastometer	(6)	171./sec.	Piston type, size of die uncertain.
—	Williams plastometer	(8)	0.021/sec.	After 1 min. compression.
—	Williams plastometer	(8)	0.067/sec.	After 5 min. compression.
Van Rossem and Van der Meijden[8]	Goodrich type plastometer	(9)	0.053/sec.	After 1 min. compression.
Van Rossem and Van der Meijden[8]	Goodrich type plastometer	(9)	0.022/sec.	After 10 min. compression.
Van Rossem and Van der Meijden[8]	Goodrich type plastometer	(9)	0.016/sec.	After 20 min. compression.
—	Inner tube machine	(5)	515./sec.	$\bar{v}=20$ cm/sec., slit = 0.89 mm.
—	Tread tubing machine	(5)	32.8/sec.	$\bar{v}=18.5$ cm/sec., slit = 1.3 cm.
Dillon	Extrusion plastometer	(5)	568./sec.	Piston type.

APPARATUS

The extrusion plastometer consists essentially of a hardened steel piston which extrudes the rubber through a die at the lower end of a steel cylinder. The piston, which is of 1.27 cm ($\frac{1}{2}''$) diameter, is operated through a distance of 7.62 cm (3″) by a pneumatic piston of diameter 14 cm ($5\frac{1}{2}''$). Thus, air pressures of 0.35 to 0.56 kg/cm² (5 to 80 lb/in.²) used in the pneumatic cylinder, correspond to pressures of 42.5 to 68.0 kg/cm² (605 to 9680 lb/in.²) exerted on the rubber. The inner diameter of the extrusion cylinder was made 1.59 cm ($\frac{5}{8}''$) to avoid the jamming which might occur with a snugly fitting piston. The extrusion cylinder was heated electrically. A coil of No. 40 B & S nickel wire was wound underneath the nichrome heating windings, and served as a resistance thermometer. The temperature was controlled manually to within 0.1°C by manipulating a rheostat in the heating circuit so as to maintain balance in a Wheatstone bridge, one arm of which was the nickel resistance coil. An additional heating coil wound below the die served as a guard ring in preventing downward heat flow across the die. The whole extrusion unit was carefully insulated thermally by means of Bakelite and felt.

The air pressure for operating the pneumatic piston was maintained constant to within 0.017 kg/cm² ($\frac{1}{4}$ lb/in.²) by means of a common type of reducing valve. To further stabilize the pressure at high extrusion velocities, a 75.7 liter (20 gal.) steel tank was connected to the air line near the plastometer air inlet. Small tubing and constrictions were avoided as far as possible, in order to reduce pressure drops. Pressures were measured by a gauge of the Bourdon tube type.

The orifice (see Fig. 1) was 3.18 mm ($\frac{1}{8}''$) in diameter, and 4.76 mm ($\frac{3}{16}''$) in length. Its upper end was tapered by means of a 45° cone up to the diameter of the extrusion cylinder. The die plate and the extrusion cylinder were pinned together so as to prevent relative motion but to permit quick removal from a yoke which was rigidly attached to a table. The pneumatic cylinder unit and the extrusion piston were screwed into the top of the yoke by means of a pair of helical planes. Smooth ground surfaces on both ends of the extrusion cylinder prevented leakage of rubber.

At the lower rates of flow, the time of extrusion was measured by means of a stop watch. At the higher rates, a contact device mounted on the tail rod of the pneumatic unit closed an electric

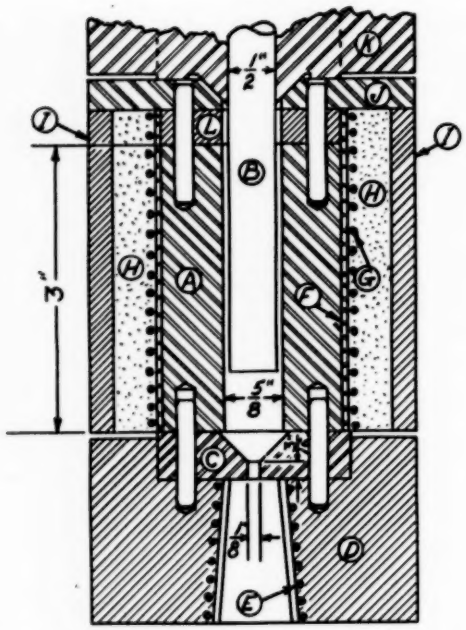

FIG. 1. Detail of extrusion unit. *A*, extrusion cylinder; *B*, extrusion piston; *C*, die plate; *D*, Bakelite base; *E*, guard ring heating coil; *F*, nickel resistance coil; *G*, nichrome heating coil; *H*, felt insulation; *I*, Bakelite tube; *J*, steel plate; *K*, rotating upper unit; *L*, Bakelite shim.

circuit at 6 equally spaced points in the stroke, thus actuating an induction coil. The high potential terminal of this coil was connected to a stationary electrode pressed against a sheet of polar coordinate paper fastened on a brass disk which was rotated at 1 r.p.m. by a synchronous motor. Thus at 6 equally spaced points of the stroke, a small hole was burned in the coordinate paper. From this series of points, the total time of extrusion, and the degree of uniformity of the extrusion velocity were known.

Extruded samples were weighed to within 0.01 g and, from the specific gravity of the stock, the extruded volume was computed. The rate of efflux was then calculated as the quotient of the volume extruded and the time of extrusion.

For loading the cylinder, rubber pellets were cut out by means of a rotating cylindrical cutter. This cut the samples in the form of a cylinder of 1.51 cm ($\frac{19}{32}$") diameter and length limited only by the thickness of the sheet of rubber from which they were cut. These samples slipped readily into the 1.59 cm ($\frac{5}{8}$") bore of the extrusion cylinder.

For all the stocks thus far tested, the rubber was found to come up to temperature in 20 minutes or less. Hence, this heating time was adopted as a standard. When only a few extrusions were to be made, the rubber was placed in the cylinder and allowed to stand at the desired temperature for 20 minutes without additional preheating. When it was desired to run a large number of samples, they were conditioned in oil-tight sheet metal air chambers mounted in a thermostatically controlled oil bath, set at the correct temperature, for 20–40 minutes and then transferred quickly to the extrusion cylinder where they were kept for 8–10 minutes to compensate for any temperature drop during transfer.

PROCEDURE

After the preheated rubber samples were transferred to the extrusion cylinder and tamped in so as to fill it completely, the pneumatic unit was put in place. After six minutes of standing in the cylinder, the piston was slowly lowered so as to extrude a short segment of rubber and squeeze out most of the air occluded in the rubber. After one or two minutes, the time allowed to compensate for any small departure from thermal equilibrium caused by the motion of the piston, air was admitted to the upper end of the pneumatic cylinder and the extrusion was made, the time of extrusion being recorded. Immediately after the extrusion, the air was admitted to the lower end of the pneumatic cylinder, to raise the piston. The pneumatic unit was then removed, the annulus of rubber remaining in the cylinder was pulled out by means of a hook, and the extruded segment was removed. The length of the extruded segment was measured before cooling. The measurement of length gives an inverse measure of the amount of recovery.

RESULTS

It is now quite generally conceded that there are at least two quantities necessary to define the plastic state of a material, i.e., the mobility μ ($\equiv 1/c$ in Eq. (2)) and the yield stress f. In general, for a given material, both μ and f are functions of temperature. The method used for studying the dependence of these quantities[13] on

[13] It should be noted that, because of slippage and the

the other variables (i.e., type and degree of rubber pigmentation, degree of breakdown of the rubber, etc.) was that of measuring the rate of efflux as a function of driving pressure at constant temperature.

Highly compounded stocks, such as tread stocks, were found to give simpler flow relations than lightly compounded stocks (tube stocks) or crude rubber. Hence, the various types of stocks are discussed in the order of the simplicity of the laws of flow which they obey, rather than in the order of the degree of compounding.

The curves giving the rate of efflux E as a function of pressure P for the moderately hard tread stock No. 1 (carbon black 24.4 percent by volume on rubber, accelerator-mercaptobenzothiazole) are shown in Fig. 2.

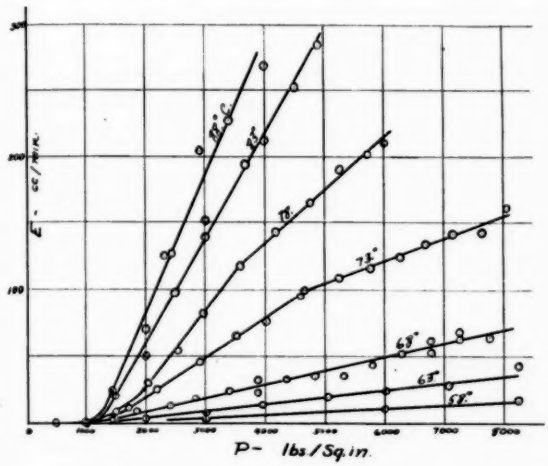

FIG. 2. Efflux rate as a function of pressure. Tread stock No. 1.

It is seen that the isothermals attain linearity at rather low pressures. The slopes of the various isothermals are radically different, showing that the mobility μ is a rapidly increasing function of temperature. A slight change in slope of the linear portions of the 73°C and 78°C isothermals is quite definite, and is reproducible, but is yet to be explained. The curves of Fig. 2 are typical of those for all tread stocks tested, except that the anomalous change in slope does not always appear.

residual elasticity of the rubber, the absolute values of μ and f cannot be calculated from the efflux rate-pressure curves and no attempt was made to obtain numerical values for either quantity.

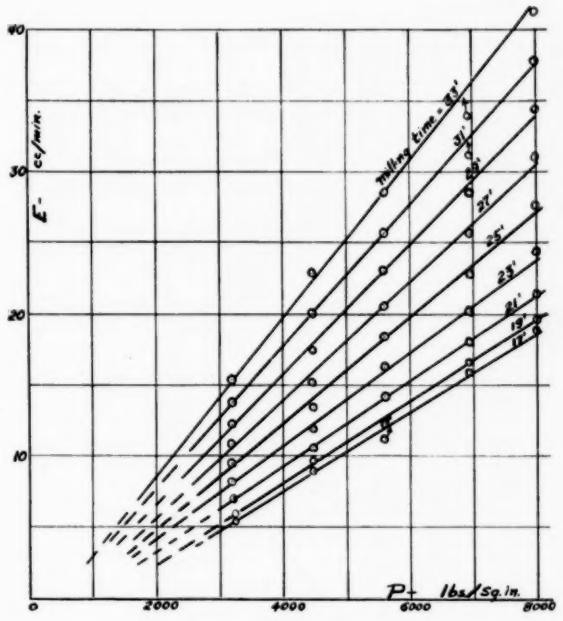

FIG. 3. Efflux rate as a function of pressure. Tread stock No. 2. Temperature 78°C.

The curves of Fig. 3 were obtained from samples taken off the mill after different periods of the mixing of a single batch of tread stock No. 2 (carbon black 26.1 percent by volume on rubber, accelerator-mercaptobenzothiazole). All the observations were made at 78°C in this case. Linearity at higher pressures again appears.

Fig. 4 is a set of E-P isothermals for a gray tube stock No. 1 (blanc fixe—3.2 percent by volume on rubber, accelerator-aldehyde amine). The curves are distinctly different from those obtained with tread stocks, for linearity is reached only at much higher pressures. Furthermore, after reaching linearity, the curves become nearly parallel. The curves for crude rubber which had been milled, cooled and then remilled (Fig. 5) show this effect in a still more pronounced form.

This parallelism of the linear portions of the E-P curves for tube stocks and crude rubber at first suggested that the die, which was only 4.76 mm ($\frac{3}{16}''$) in length, behaved as an orifice in regard to these softer stocks rather than as a tube. To investigate this possibility, a new die was made, of the same diameter 3.18 mm ($\frac{1}{8}''$) but 17.4 mm ($\frac{11}{16}''$) in length. As can be seen from

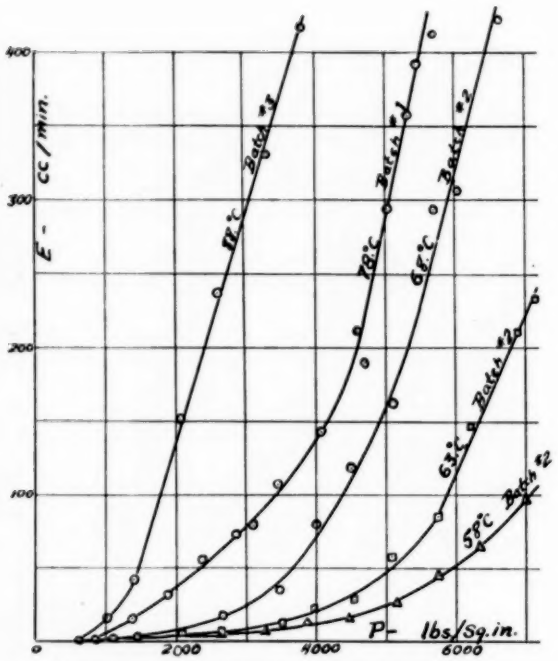

FIG. 4. Efflux rate as a function of pressure. Tube stock No. 1 (gray).

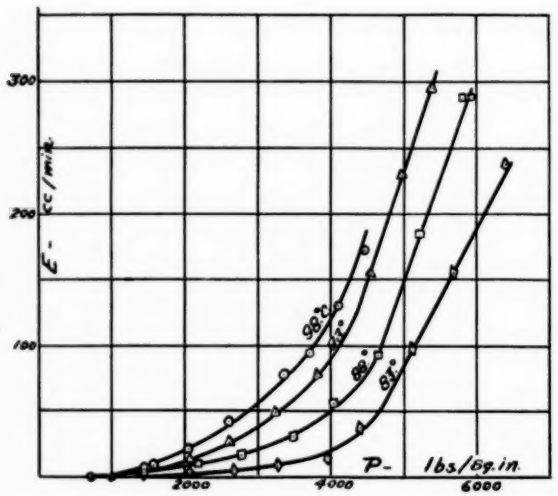

FIG. 5. Efflux rate as a function of pressure. Crude rubber (mill massed).

Figs. 6 and 7[14] no great change in the form of the E-P curves was observed with the longer tube. The parallelism of the linear portions of the curves is preserved with the longer tube, though

[14] The curves of Fig. 7 apply to a red tube stock No. 2 (blanc fixe—7.1 percent by volume on rubber, accelerator diphenyl-guanidine).

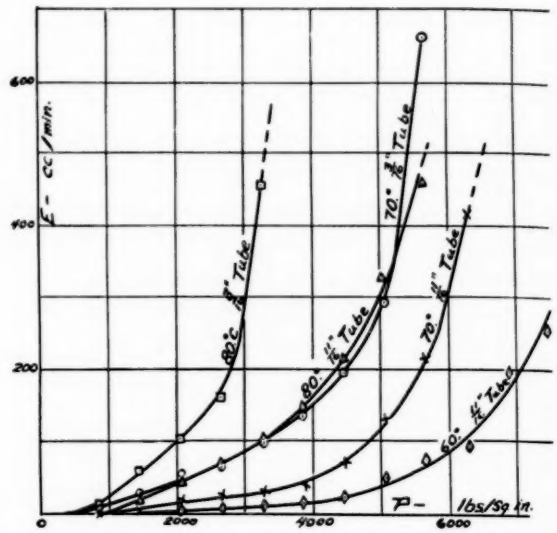

FIG. 6. Efflux rate as a function of pressure. Tube stock No. 1.

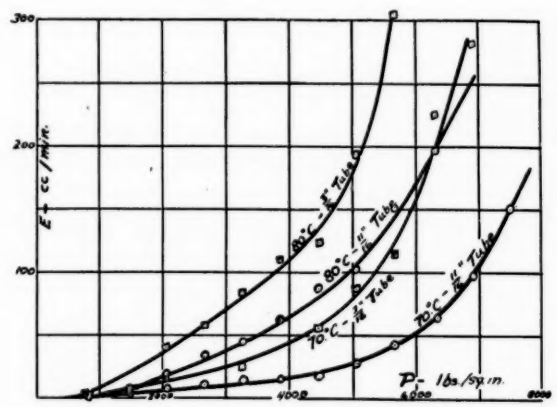

FIG. 7. Efflux rate as a function of pressure. Tube stock No. 2 (red).

the slope is slightly different for the two dies. It seems fair, then, to consider this type of curve to be characteristic of the softer stocks and to depend only slightly upon the type of die used. The ordinates are diminished considerably with the longer tube but not in the ratio of the lengths of the respective tubes. Thus it appears that a large fraction of the shear occurs in the rubber as it flows in the conical entrance to the die tube.

The peculiar form of the E-P curves for soft stocks may be interpreted to mean that the mobility is independent of temperature, at least in the region of rates of shear described by the

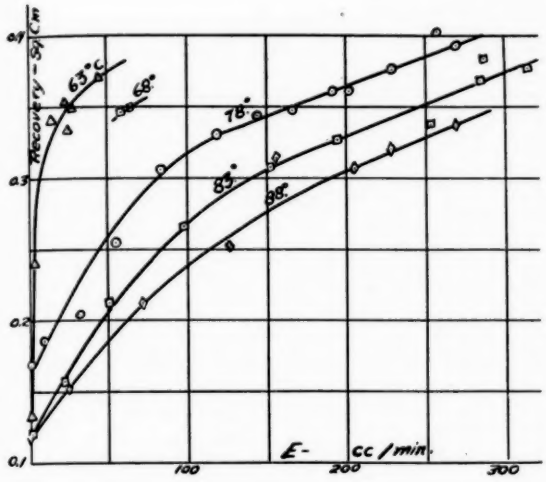

FIG. 8. Recovery as a function of efflux rate. Tread stock No. 1.

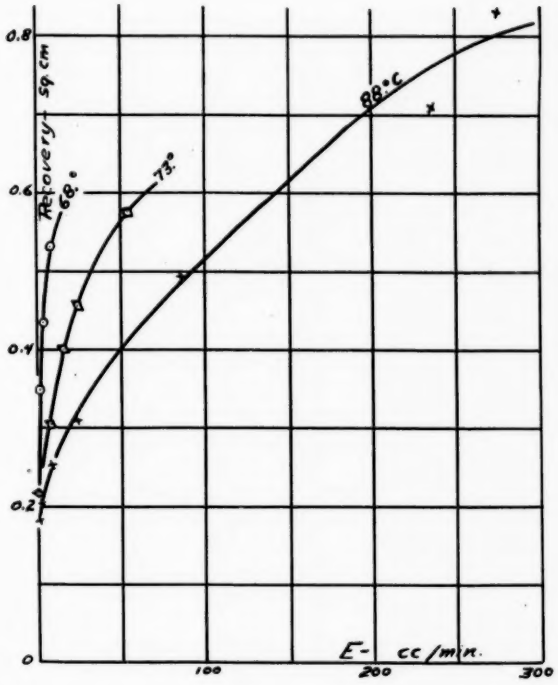

FIG. 9. Recovery as a function of efflux rate. Tube stock No. 1.

linear portions of the curves. This, then, may partially explain why the compression type plastometer, which measures the mobility at low rates of shear, often fails to correlate with factory extrusion machines employing a high rate of shear.

The relation between "recovery" and rate of efflux is given in Figs. 8, 9 and 10. "Recovery" is defined as proportional to the average cross-sectional area of the extruded segment. The length of each segment was measured immediately after extrusion and, from knowledge of the mass extruded and the specific gravity, the average cross-sectional area was computed. The curves are all of the same type, recovery increasing with rate of efflux and decreasing with temperature.

A somewhat more practical study was made with the plastometer in investigating the rate of efflux as a function of milling time. For this purpose, rubber batches were mixed on the factory 214 cm (84") mills according to standard factory specifications except that the milling was carried much beyond the standard time. Counting zero milling time as that time at which the first of the master batches was thrown on the rolls in the case of the compounded stocks, and as the time at which the unmilled crepe was thrown on, in the case of the crude rubber, samples were cut off at the intervals indicated

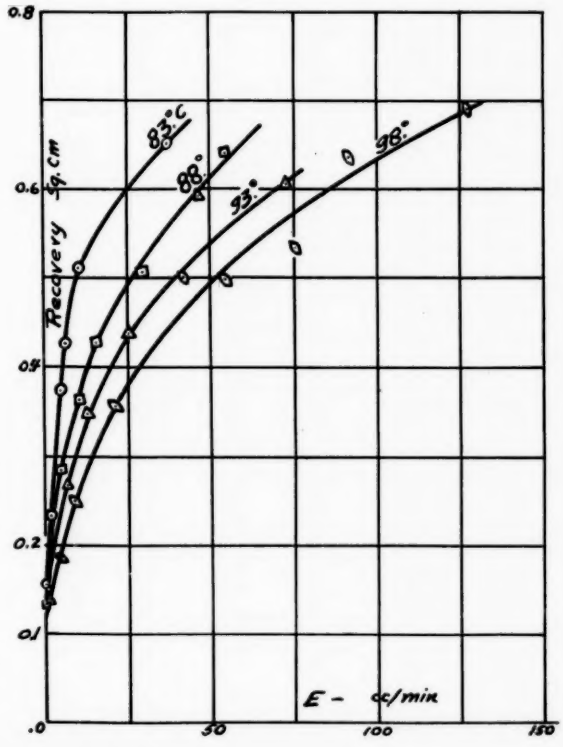

FIG. 10. Recovery as a function of efflux rate. Crude rubber (mill massed).

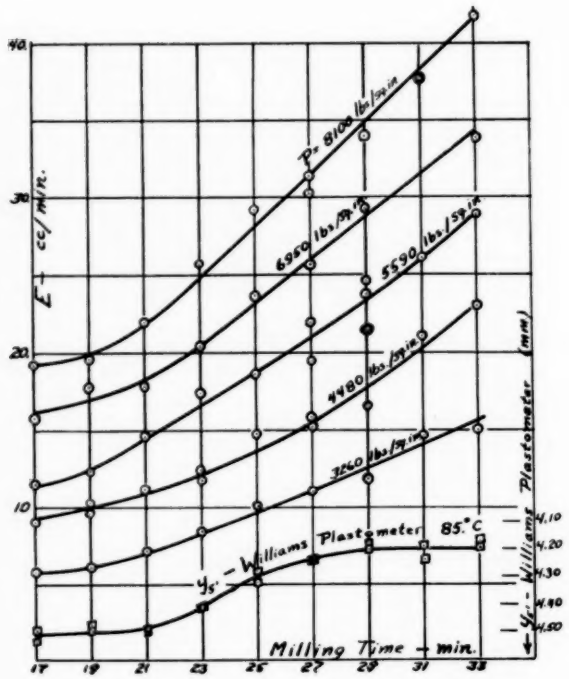

FIG. 11. Efflux rate as a function of milling time. Tread stock No. 2. Temperature 78°C.

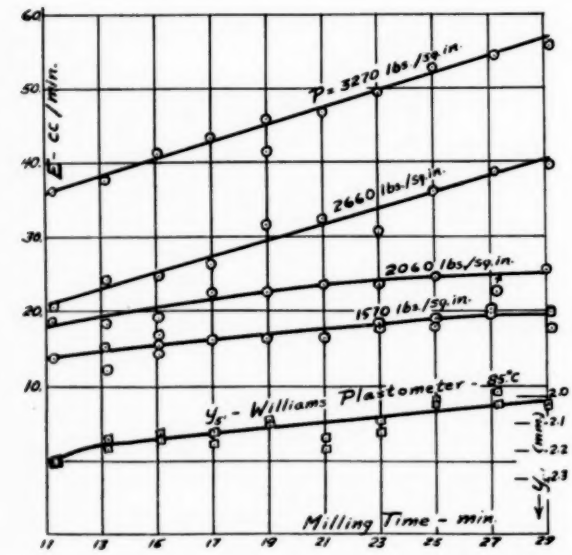

FIG. 12. Efflux rate as a function of milling time. Tube stock No. 1. Temperature 68°C.

in Figs. 11, 12 and 13. The stock was allowed to cool in flat sheets in air for one hour. Observations were then made both with the extrusion plastometer and the Williams instrument.

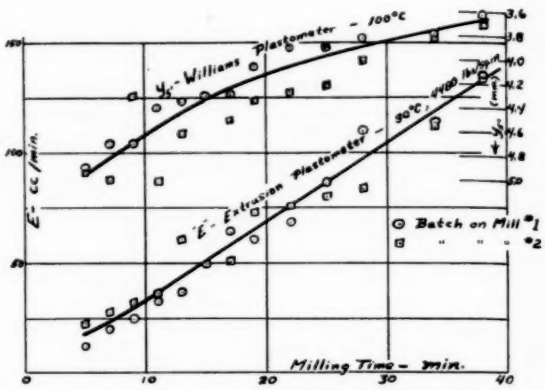

FIG. 13. Efflux rate as a function of milling time. Crude rubber.

The efflux-rate *vs.* milling-time curves for the extrusion plastometer are all of similar nature, showing a rapid and nearly linear increase of efflux rate with milling time. For tread stocks, the curve for the Williams plastometer flattens out at higher milling times. This same tendency is exhibited for crude rubber but not to so great a degree. The curves demonstrate that the extrusion plastometer, when operated at sufficiently high pressures, is more sensitive than the Williams plastometer in detecting "overmilling." Furthermore, the extrusion instrument is more sensitive to overmilling in tread stocks than in tube stocks.

SOURCES OF ERROR

1. Regularity of the flow

In computing the mean rates of shear in this work, a velocity front of parabolic section was assumed. Because of the deformation which the rubber undergoes in the extrusion cylinder before entering the die, it did not seem possible to determine experimentally the shape of the velocity front. However, a simple experiment was performed which shows that the flow is regular and is symmetrical about the axis of the die tube. The experiment consisted in placing thin calendered white stock between the pellets of tread stock or red tube stock before they were inserted in the extrusion cylinder. The stock was extruded and cured, after which it was cut along its axis. Fig. 14 is a photostat of four of these laminated extrusions, two of which (c and d) are of tread stock and two of red tube stock (a and

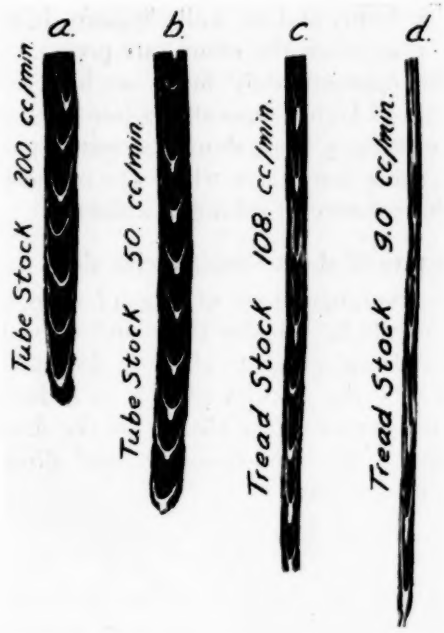

FIG. 14. Photostat of laminated extrusions to show regularity of the flow.

b). To draw conclusions from these flow figures other than that the flow is regular and symmetrical about the axis of the tube seems unjustified.

2. Correction for friction in the pneumatic unit

The ratio of the area of the pneumatic piston to that of the 1.27 cm ($\frac{1}{2}''$) piston is $(14.0/1.27)^2 = 121$. Hence, if there were no friction in the pneumatic unit, for a given efflux rate E, the pressure on the rubber would be

$$P_E = 121 \cdot P_E' \qquad (11)$$

where P_E' is the pressure gauge reading. For the actual case where there is a frictional force equivalent to a back pressure P_E'',

$$P_E = 121 \cdot (P_E' - P_E''). \qquad (12)$$

The quantity P_E'' was determined by running the plastometer with no rubber in the extrusion cylinder, at low air pressure, measured both by the gauge and by a mercury manometer, and measuring the velocity of the piston with the timing device. A curve was plotted giving the observed values of P_E'' as a function of E. Thus, for any efflux rate E, the proper value of P_E'' could be read from the curve and subtracted from the observed gauge reading to give the pressure on the rubber by Eq. (12).

3. Effect of shear in rubber annulus between piston and inner wall of extrusion cylinder

The diameter of the extrusion piston was made 3.18 mm ($\frac{1}{8}''$) less than that of the extrusion cylinder, so as to avoid "jamming" at high pressures. This could occur with a tightly fitting piston, particularly when using heavily compounded stocks. Consequently, there was reason for some concern as to whether or not a large fraction of the total shearing force was used in shearing the rubber annulus between the piston and the inner wall of the cylinder.

Suppose the whole of the shearing force were utilized in shearing the rubber in the annulus. Then the velocity of the piston would continuously decrease during the extrusion because of the linear increase of shearing area between piston and cylinder. For the actual case, where part of the force shears the rubber in the annulus and part extrudes the rubber through the die, the distribution of the total force between the annulus and the extruding rubber can be computed by measuring the velocity at several points in the stroke. Using the results of a large number of extrusions (as recorded by the timing device), it was thus found that not more than 15 percent of the total force was utilized in shearing the rubber annulus.

4. Effect of premature vulcanization in the extrusion cylinder

For all the stocks employed in this work, careful observations were made of the extrusion rate as a function of time of heating. No decrease in the extrusion rate was observed in the standard preheating time (20 minutes) and hence it may be concluded that the effect of premature vulcanization, for these stocks, was negligible.

MATHEMATICAL APPENDIX

For an accurate derivation of the mean rate of shear in a material flowing through a tube or orifice, it is necessary to know (a) the form of the velocity front and (b) the degree of slip at the walls. The flow conditions for rubber in the plastometer, which has been described, are

somewhat complex since rubber stocks possess considerable elasticity. Furthermore, the degree of slip has not, as yet, been investigated. When the mean rate of shear is computed from the equation of plastic flow which embodies the idea of plug flow as suggested by Buckingham, i.e.,

$$v=\mu[(P/4L)(R^2-r^2)-f(R-r)],$$

where v is velocity of plastic material at a distance r from the axis of the tube, R is the radius of the tube, L is the length of the tube, μ is the mobility, and P the applied pressure, dv/dr is given as a function of f, μ, P, L, R and the maximum velocity of flow v_m. Since f is very difficult to determine in rubber, because of the presence of elasticity and slip and, in fact, has little meaning for tube stocks and crude rubber, the resulting formula for dv/dr is of little practical use. Hence, to obtain an approximate formula for dv/dr, it was necessary to assume a parabolic velocity front, and no wall slippage. It may be noted that, since the efflux rate-pressure curves become approximately linear at high rates of flow and at high temperatures (see Figs. 2, 3, 4, 5), the velocity front should be nearly parabolic under those conditions which are of most practical importance in tubing machines.

Mean rate of shear—rectangular slit

For a rectangular slit of length l, then, assuming a parabolic velocity front and no wall slippage, and neglecting the shear at the ends of the slit, if v be the velocity of flow at a distance x from the center of the slit, v_m be the maximum velocity, h the semi-cross-sectional dimension, and k a constant;

$$v=k(h^2-x^2), \quad v_m=kh^2.$$

Here, the factor $A(x, t)dx$ of Eq. (3) is $vtldx$ and the volume-weighted mean rate of shear is:

$$s_{ave}=-\left(\frac{dv}{dx}\right)_{ave}=\frac{t\cdot l\int_0^h-(dv/dx)vdx}{t\cdot l\int_0^h vdx}=\frac{\int_0^h 2x\cdot k\cdot(h^2-x^2)dx}{\int_0^h k\cdot(h^2-x^2)dx}=\frac{3}{4}\frac{v_m}{h}. \tag{4}$$

Now, to put s_{ave} in terms of the mean velocity v_{ave}, we write

$$v_{ave}=\frac{\int_0^h vdx}{\int_0^h dx}=\frac{\int_0^h k(h^2-x^2)dx}{h}=\frac{2}{3}v_m. \tag{5}$$

Thus:

$$s_{ave}=-(dv/dx)_{ave}=(9/4)v_{ave}/D, \tag{6}$$

where $D=2h$.

Mean rate of shear—circular orifice

Assuming that the velocity front is a paraboloid of revolution and that there is no wall slippage, if h be the radius of the tube;

$$v=k(h^2-r^2);\ v_m=kh^2.$$

Here, for volume weighting, the factor $A(x, t)dx$ is $2\pi\cdot r\cdot v\cdot t\cdot dr$. Thus:

$$s_{ave}=-\left(\frac{dv}{dr}\right)_{ave}=\frac{2\pi t\int_0^h-(dv/dr)v\cdot rdr}{2\pi t\int_0^h v\cdot r\cdot dr}=\frac{\int_0^h 2r^2(h^2-r^2)dr}{\int_0^h r(h^2-r^2)dr}=\frac{32}{15}\frac{v_m}{D}, \tag{7}$$

where $D=2$h. The mean velocity, weighted by the element of cross-sectional area, is

$$v_{ave}=\int_0^h v\cdot rdr/\int_0^h r\cdot dr=\int_0^h k(h^2-r^2)rdr/\tfrac{1}{2}h^2=\tfrac{1}{2}v_m. \tag{8}$$

Thus:

$$s_{ave}\equiv-(dv/dr)_{ave}=(64/15)v_{ave}/D. \tag{9}$$

Mean rate of shear—Williams parallel plate plastometer

Consider the flow of plastic material between parallel plates when the separation at time t is y, the radius of the pellet being r. The flow may be considered as extrusion through a rectangular slit of continuously decreasing width and increasing length. If we assume a parabolic velocity front, no slip at the plates, and Williams equation[10]

$$yt^n = K \tag{16}$$

where K and n are constants, we obtain upon differentiating with respect to t,

$$v_y = dy/dt = -ny/t = -nK/t^{n+1}, \tag{18}$$

which is the velocity of the moving plate. Now, to calculate the radial velocity v_r, we consider the pellet as a circular disk. Then the volume of the disk is

$$V = \pi r^2 y = \text{const.}$$

Then

$$dV = 2\pi r y dr + \pi r^2 dy = 0$$

or

$$v_r = \frac{dr}{dt} = -\frac{r}{2y}\frac{dy}{dt} = \frac{n}{2}\frac{r}{t} = \frac{n}{2}\left(\frac{V}{\pi}\right)^{\frac{1}{2}}\frac{1}{y^{\frac{1}{2}} \cdot t}.$$

Hence, the mean velocity of the rubber at the periphery is

$$v_{ave} = v_r = \frac{n}{2}\left(\frac{V}{\pi}\right)^{\frac{1}{2}}\frac{1}{y^{\frac{1}{2}} \cdot t}. \tag{19}$$

From Eq. (6) for a static slit orifice, the rate of shear is given as a function of y and t. Thus

$$s_{ave}(y, t) = -\left(\frac{dv}{dy}\right)_{ave} \frac{9}{4}\frac{v_{ave}}{y} = \frac{9}{4}\frac{n}{2}\left(\frac{V}{\pi}\right)^{\frac{1}{2}}\frac{t^{3n/2-1}}{K^{\frac{1}{2}}}. \tag{21}$$

Williams[10] gives $n \leqq 0.2$, so that the mean rate of shear over the periphery of the pellet is

$$s_{ave}(t) \leqq \frac{9}{8}\frac{k}{K^{\frac{1}{2}}}\left(\frac{V}{\pi}\right)^{\frac{1}{2}} t^{-0.7} = \frac{9}{8}\left(\frac{V}{\pi}\right)^{\frac{1}{2}}\frac{n}{K^5}\frac{y^4}{y^{\frac{1}{2}}}. \tag{8}$$

Mean rate of shear—Goodrich type parallel plate plastometer

Consider the flow of a pellet of radius R of plastic material between plates of radius R with a separation y at time t. If we assume a parabolic velocity front, no slip at the plates, shear negligible in the bulged portion, i.e., $R = \text{const.}$ and Taylor's equation[7]:

$$1/y^2 - 1/y_0^2 = kt \tag{23}$$

where y is the final thickness of pellet at time t, y_0 the initial thickness of pellet at time o, $k \equiv 4\ mg/3\eta\pi(2R)^4 \equiv \text{const.}$, mg the downward force on top plate, η the viscosity of rubber; we have, upon differentiating with respect to t,

$$dy/dt = -ky^3/2, \tag{25}$$

so, if the volume of the disk is $V = \pi R^2 y$,

$$dV = \pi R^2 dy. \tag{26}$$

The rate of efflux is

$$dV/dt = \pi R^2 dy/dt = -(v_r)_{ave} 2\pi R y, \tag{27}$$

where $(v_r)_{ave}$ is the mean radial velocity of the rubber. Hence, from (27) and (25),

$$(v_r)_{ave} = Rky^2/4. \tag{28}$$

The flow, for this instrument, is roughly equivalent to extrusion through a rectangular slit of varying width but constant length. Thus, we can use again expression (6) to obtain the mean rate of shear

$$s_{ave}(y) = -(dv/dx)_{ave} = 9(v_r)_{ave}/4y = 9Rky/16 \tag{29}$$

or, from (23),

$$s_{ave}(t) = (9Rk/16)1/(kt + 1/y_0^2)^{\frac{1}{2}}. \tag{10}$$

The value of k is found by plotting t against $1/y^2$, using experimental data. The slope of the linear curve obtained is then $1/k$.